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FINAL REPORT

STUDY TO ASSESS THE IMPACT OF TOXIC PROPELLANTS ON KSC ECOLOGY

DECEMBER 1966
CONTRACT NAS10 - 3147

PREPARED FOR: JOHN F. KENNEDY SPACE CENTER
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
COCOA BEACH, FLORIDA

TRW SYSTEMS ...IDA OPERATIONS
7001 NORTH ATLANTIC AVENUE • CAPE CANAVERAL, FLORIDA

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Contract NAS10-3147

Prepared for

John F. Kennedy Space Center
National Aeronautics and Space Administration
Cocoa Beach, Florida

December 1966

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Program direction and the portions of the program related to nitrogen tetroxide were performed by TRW Systems under the direction of G. N. Woodruff, Project Manager.

ABSTRACT

This study, conducted under Contract NAS10-3147, with the John F. Kennedy Space Center studied the impact of toxic propellants on plant species on and near KSC.

Nitrogen tetroxide which is currently used as an oxidizer, and hydrogen fluoride which would be the toxic vapor from a fluoride-based oxidizer, were the propellants studied. This study was concerned only with high vapor concentration, short duration exposures which might result from launch operations.

The vapors of both propellants caused plant damage in proportion to the vapor concentration and exposure time. Boundary conditions for damage by NO_2 varied from 25 ppm for four hours to 250 ppm for 15 minutes. Boundary levels for HF ranged from 15 ppm for two hours to 8 ppm for four hours.

The minimal effects of both vapors on plant tissue resemble the symptoms produced by environmental stresses, insects and diseases. The maximum effects observed included complete defoliation, abscission of flowers and fruits and necrosis of terminal shoots. Vapor concentrations and/or exposure time significantly above the maximum levels studied in this program could be expected to produce complete necrosis of plants.

HF was approximately 20 times more effective on a concentration basis than NO_2 in inducing plant damage. Plant damage induced by HF can be distinguished from that induced by NO_2 on the basis of the species affected, type of tissue injured, pattern of symptom development and expression, and chemical analyses.

Injuries to plants observed in this study ranged from marginal effects through complete defoliation. The visible expressions of injury are described for a number of citrus varieties and ornamental species.

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1.0 INTRODUCTION

This study was conducted to determine the effects of short-term, high concentrations of NO_2 and HF vapor on plant life in and around the KSC area. The plants growing in that area were identified and a series of preliminary fumigations were conducted to determine the relative sensitivity of a number of these plants to injury by propellant vapors.

Six citrus varieties and six ornamental species were selected from this screening and exposed to propellant vapors at various time-concentrations. The visible expressions of injury were documented and foliar analyses of plant tissue conducted to obtain correlation data between conditions of exposure and foliar accumulation.

RESULTS AND CONCLUSIONS

The results of these fumigations show that even short-term exposures to HF or NO_2 will cause significant injury to plants. Concentrations of HF well below those tolerated by humans or animals will cause dramatic plant injury in less than eight hours. Concentrations of NO_2 which cause plant injury for short-term exposures are well above the maximum allowable concentrations for humans.

Relatively low levels of HF or somewhat higher levels of NO_2 will result in identifiable plant damage. If threshold concentrations or exposure times are exceeded, the damage will include defoliations, necrosis, and chlorosis of the tissues. This can be expected to result in partial or complete loss of the crop for the year.

RECOMMENDATIONS

This study did not assess the long-term significance of these exposures. Since fluoride, unlike NO_2, accumulates in the foliage of plants, it is possible that even a single exposure to HF would result in the absorption of enough fluoride in plant tissue to affect subsequent growth. Therefore, further study to assess the long-term effects on plants of acute exposure to

HF is required before definitive estimates of the total extent of the injury can be made. Since a study of long-term effects requires several years, it is recommended that this be given attention well in advance of any proposed use of fluorine oxidizers.

Monitoring instrumentation sensitive to low levels of HF will be required in the field whenever and wherever fluorine oxidizers are employed. The instrumentation suitable for detecting vapor hazards to personnel is not sensitive enough to detect hazards to plants. This, too, should receive attention well in advance of the use of fluorine.

2.0 FIELD SURVEY

2.1 INTRODUCTION

The presence on the Merritt Island Launch Area of numerous citrus groves which are owned by the Government but leased to commercial interests was one factor which influenced initiation of this program. These groves, many of them in close proximity to the launch area, would receive the heaviest dosage of propellant vapors in the event of a spill or incident. A 15-mile radius from Launch Complex 39 includes not only those leased groves, but additional citrus acreage on Merritt Island and ornamental plantings surrounding dwellings on both Merritt Island and the Florida mainland.

A field survey was conducted of this area and conversations were held with the County Agricultural Agent and others to determine which plants (both citrus and ornamentals) should be considered for the experimental program. A further object of the field survey was to determine some of the environmental factors present in the area which might contribute to changes in sensitivity of vegetation to propellant vapors.

2.2 CITRUS VARIETIES

Citrus varieties present within the area under consideration included Valencia, Hamlin, Tangelo, Temple and Pineapple Oranges and Marsh Seedless Grapefruit. Other citrus plantings of Navel Oranges, Tangerines and Duncan Grapefruit are present in the area. These varieties which include the fancy fruits for gift shipments are not as extensively planted as the six varieties first mentioned.

2.3 ORNAMENTAL SPECIES

Ornamentals within the area include most of the subtropical species common to the Florida east coast. These are present as dooryard plantings principally on the Florida mainland, although a few residential areas are on Merritt Island adjacent to the KSC facility. No effort was made to identify the occasional plantings of specimen or rare plants which might be included within this area.

The principal species of ornamentals found in this area included:

Allamanda (Allamanda cathartica)
Australian Pine (Castanospermum australe)
Azalea (Rhododendron canescens)
Barbados Cherry (Malpighia glabra)
Bougainvillea (Bougainvillea spectabilis)
Boxwood (Buxus microphylla)
Carissa (Carissa carandas)
Croton (Codiaeum variegatum)
Flame Vine (Pyrostegia ignea)
Gardenia (Gardenia radicans)
Hibiscus (Hibiscus rosa-sinensis)
Ixora (Ixora coccinea)
Jacaranda (Jacaranda acutifolia)
Jasmine (Gardenia radicans)
Juniper (Juniperus conferta)
Ligustrum (Ligustrum lucidum)
Melaleuca (Melaleuca leucadendra)
Oleander (Nerium oleander)
Pittosporum (Pittosporum tobira)
Poinsetta (Euphorbia pulcherrima)
Pyracantha (Pyracantha coccinea)
Rose of Sharon (Hibiscus syriacus)
Sea Grape (Coccolobis uvifera)
Slash Pine (Pinus caribaea)
Turks Cap (Malvaviscus arboreus)
Viburnum (Viburnum)

Annuals and herbaceous perennials were not considered to possess sufficient economic importance to warrant study or listing.

2.4 ENVIRONMENTAL AND CULTURAL CONDITIONS

In studying the conditions present in the area which might predispose vegetation to injury by toxic propellants, principal attention was paid to the commercial citrus acreage on and near MILA. Dooryard plantings of

ornamental species are subject to extremes in care and culture, depending upon the whims of the property owner, and no generalization as to condition of ornamental plantings would be valid. The commercial citrus groves are, however, systematically maintained by the owners or by commercial grove caretaking companies. Unfortunately, this maintenance is not uniform, with the result that a wide variety of nutritional disorders, insect damage and plant diseases can be found in the groves within the area. Of these, nutritional disorders would be the important factor which might predispose plants to injury by air pollution.

Within the area, groves which were not well maintained showed clear evidence of boron and manganese deficiencies on grapefruit and iron and magnesium deficiencies on all citrus varieties.

The plant is a complex biological system controlled by the interaction of genetic and environmental factors. Therefore, the status of the plant and the quality of its environment must be considered in any evaluation of the effects of air pollutants on vegetation. Both factors must be considered for two basic reasons. First, the response of the plant to the pollutant will be modified or be dependent upon these factors. Second, environmental effects can resemble chronic or residual effects of air pollutants. Nutritional status is known to affect the metabolic responses,[1] the reproductive processes[2] and the appearance of foliar injuries in HF-fumigated plants. Moreover, the pattern induced by chronic HF exposure is indistinguishable from symptoms of manganese deficiency and, in certain cases, from iron chlorosis or water stress. The effect of mineral nutrition on NO_2-fumigated plants is not known.

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[1] Applegate, H.D., and D. F. Adams, Nutritional and Water Stress on Fluoride Susceptibility on Bean Seedlings. Phyton 14: 111-120. 1960.

[2] Pazk, Merrill R., Response of Tomato Fruiting to Hydrogen Fluoride as Influenced by Calcium Nutrition. J. Air Pollution Cont. Assoc. 16: 541-544. 1966.

3.0 PRELIMINARY SCREENING TO DETERMINE EXPOSURE LEVELS

3.1 INTRODUCTION

Phase I plant fumigations were designed to determine for gaseous hydrogen fluoride (HF) and nitrogen dioxide (NO_2), the range of concentration x duration exposures necessary to induce visible plant responses ranging from no injury to severe damage.

Two citrus varieties (Hamlin and Valencia oranges) and two ornamental species (Ixora coccinea and Hibiscus rosa-sinensis) that are commonly grown in Brevard County, Florida, were selected for these initial screenings. Two plants of each species or variety were subjected to each of the 30 exposures listed in Table 1. Plant injury was determined by post-fumigation observations of each plant.

3.2 HYDROGEN FLUORIDE

The 18 HF exposures in Phase I ranged from an exposure value (expressed as concentration x duration) of 0.5 ppm·hrs. (0.5 ppm. HF for one hour) to 40 ppm·hrs. (10 ppm. for four hours). The lowest exposure was not injurious to Valencia orange trees or to Ixora or Hibiscus plants, but slight tip and marginal chlorosis was induced on approximately 20 per cent of the young leaves of Hamlin orange trees. The most acute exposure resulted in damage to all plants. Complete defoliation of young leaves, necrosis of succulent shoots, abscission of all young fruit, and moderate intercostal necrosis of the older foliage of both citrus varieties were observed. All Hibiscus leaves were severely necrotic, brown, and desiccated; nevertheless, they did not defoliate. Foliar necrosis of Ixora plants was most pronounced at the terminal portions of stems and became generally less severe toward the base of the plants. Many of these symptoms were evident within one hour after fumigation.

Exposure values between these extremes resulted in plant injury of intermediate severity. In general, visible symptoms of injury tended to become more pronounced when plants were exposed to HF for a longer period of time, or to a higher concentration, or both.

The relative sensitivity of the four plants to HF in Phase I fumigations was as follows:

Hamlin orange > Valencia orange > Hibiscus > Ixora

The progressive development of injury symptoms is described in detail for Phase III fumigations and will not be discussed here.

3.3 NITROGEN DIOXIDE

Exposure values of the 13 Phase I plant fumigations with NO_2 ranged from 10 ppm·hrs. (40 ppm. for 0.25 hour) to 375 ppm·hrs. (150 ppm. for 2.5 hours). However, concentrations of 25 to 250 ppm. NO_2 and durations up to eight hours were also included in these fumigations (Table 1). No visible symptoms of injury were evident on plants exposed to the lowest NO_2 exposure, but the highest exposure resulted in 90 to 100 per cent necrosis of all leaves of Hibiscus and Ixora plants. Injury to Valencia and Hamlin orange trees was severe with complete necrosis of young leaves and 90 to 100 per cent defoliation of older leaves. The remaining exposures resulted in injury between these extremes. Post-fumigation observations revealed that of the four plant species fumigated in Phase I, Hibiscus plants were the most sensitive to NO_2-induced injury and Ixora plants were the most resistant. Hamlin and Valencia orange trees were slightly less sensitive than Hibiscus plants.

TABLE 1

PHASE I FUMIGATIONS WITH HF AND NO_2 PROVIDED TO HAMLIN ORANGE, VALENCIA ORANGE, HIBISCUS, AND IXORA PLANTS

Pollutant	Concentration (ppm.)	Duration (hrs.)	Exposure (ppm·hrs.)
HF	0.5	1	0.5
	0.5	2	1
	0.5	4	2
	0.5	8	4
	1	0.5	0.5
	1	1	1
	1	2	2
	1	4	4
	1	8	8
	1.5	1	1.5
	2	2	4
	2	4	8
	3.3	0.5	1.6
	3.3	1	3.3
	5	2	10
	8	0.25	2
	8	0.5	4
	10	4	40
NO_2	25	8	200
	40	0.25	10
	50	4	200
	50	6	300
	75	0.5	37.5
	75	1	75
	100	0.25	25
	100	2	200
	150	1	150
	150	2.5	375
	200	0.5	100
	250	0.2	50
	250	0.3	75

4.0 SCREENING AND SELECTION OF ORNAMENTAL PLANTS

4.1 INTRODUCTION

A major task of this investigation was to observe and evaluate the responses of six citrus varieties and six ornamental species having varying degrees of sensitivity to HF and NO_2 (Phase III). Therefore, Phase II fumigations were designed to ascertain the relative sensitivity of a broad spectrum of ornamental species commonly grown in Central Florida from which six were ultimately selected for Phase III experiments.

Five replicate plants of each of the 16 ornamental plant species listed in Table 2 were exposed to the seven HF and nine NO_2 fumigations described in Table 3.

4.2 HYDROGEN FLUORIDE

The magnitude of HF-induced plant damage in each of the Phase II fumigations served as the criterion for ranking the 16 ornamental plant species as to their relative sensitivity to HF. The observed plant injury was divided into three arbitrary categories: (a) very sensitive, (b) moderately sensitive, and (c) relatively resistant. Within each grouping the species were ranked in order of decreasing sensitivity to HF:

Very sensitive:	(1) Azalea
	(2) Bougainvillea
	(3) Melaleuca
	(4) Pyracantha
	(5) Gardenia
Moderately sensitive:	(1) Oleander
	(2) Cape Jasmine
	(3) Pittosporum
	(4) Shore Juniper
	(5) Hibiscus
	(6) Ligustrum
	(7) Ixora

TABLE 2

ORNAMENTAL SPECIES USED IN ALL PHASE II FUMIGATIONS WITH NO_2 AND HF

COMMON NAME	BOTANICAL NAME
*Croton	Codiaeum variegatum
*Melaleuca	Melaleuca leucadendra
*Azalea	Rhododendron canescens
Bougainvillea	Bougainvillea spectabilis
Shore Juniper	Juniperus conferta
Pittosporum	Pittosporum tobira
Ligustrum	Ligustrum lucidum
*Carissa	Carissa carandas
Oleander	Nerium oleander
*Hibiscus	Hibiscus rosa-sinensis
*Ixora	Ixora coccinea
Pyracantha	Pyracantha coccinea
Gardenia	Gardenia jasminoides
Cape Jasmine	Gardenia radicans
Slash Pine	Pinus caribaea
Palmetto	Sabal Palmetto

*Species selected for Phase III fumigations.

TABLE 3

CONCENTRATION, DURATION, AND TOTAL EXPOSURE VALUES
FOR PHASE II PLANT FUMIGATIONS WITH HF AND NO_2

POLLUTANT	CONCENTRATION (ppm.)	DURATION (hrs.)	EXPOSURE (ppm·hrs.)
HF	0.3	2	0.6
	0.5	2	1
	1.5	4	6
	4	2	8
	4	2	8
	6	1	6
	8	4	32
NO_2	10	8	80
	25	6	150
	30	4	120
	40	3	120
	50	1.7	85
	100	1	100
	150	0.7	105
	200	0.3	60
	250	0.2	50

Relatively resistant:	(1) Carissa
	(2) Croton

Injury to Slash Pine and Palmetto was erratic and did not follow any pattern. Replicate plants of a given fumigation often displayed symptoms ranging from no visible injury to severe necrosis and/or complete defoliation. Furthermore, when delivered to the test site, some of these plants displayed symptoms of nutritional deficiencies and water stress. It was therefore impossible to make a valid assessment of HF-induced injury. Consequently, Slash Pine and Palmetto plants were omitted from the above rankings.

4.3 NITROGEN DIOXIDE

The 16 ornamental species were grouped and ranked as described above with respect to their relative sensitivity to NO_2 fumigations.

Very sensitive:	(1) Azalea
	(2) Oleander
	(3) Bougainvillea
	(4) Pyracantha
	(5) Hibiscus
Moderately sensitive:	(1) Pittosporum
	(2) Melaleuca
	(3) Ligustrum
	(4) Ixora
	(5) Cape Jasmine
	(6) Gardenia
Relatively resistant:	(1) Shore Juniper
	(2) Carissa
	(3) Croton

Slash Pine and Palmetto plants were not included in these rankings for the reasons described above.

4.4 NITRATE ANALYSIS

Analyses of NO_2 exposed plant tissues were desirable to determine the amount of pollutant absorbed during fumitation. Growing plants, unless maintained under conditions of severe nitrogen stress, contain relatively high concentrations of a great many nitrogen containing organic and inorganic substances. Thus, it was doubtful whether analyses for total nitrogen content of NO_2-fumigated plants would reveal any increase over the high background nitrogen content. The most logical approach was to determine changes, if any, in the nitrate nitrogen (NO_3) content.

Nitrate (NO_3) analyses of foliage samples from 11 species, representing three NO_2 fumigations (60, 120, 150 ppm·hrs) were determined by the phenoldisulfonic acid method of Harper (1924), following the modification of Blackman and Templeman (1940) for plant tissues. Equal weights (from 0.1 - 1.0 gram) of dried plant material and magnesium oxide were boiled in 100 ml. of water for five minutes to remove the ammonia-nitrogen. After cooling, 2 ml. of a saturated silver sulfate solution were added to precipitate any chlorides present. The solution was filtered, decolorized with charcoal, and made to a volume of 250 ml. with water. Three aliquots of 10 ml. each were added to evaporating pans and evaporated to dryness. The residue was dissolved in 1 ml. of phenoldisulfonic acid[1] and washed into a volumetric flask with 10 ml. of water. Ten ml. of concentrated NH_4OH diluted to 1 to 3 with water was added, and the solution was then made to 25 ml. with water and shaken for a few seconds to develop the color. The optical density was measured spectrophotometrically at 400 mμ and the μg. NO_3 was determined by reference to a standard curve prepared using KNO_3 standards.

The results of these analyses were extremely variable, and no conclusive inferences could be made. For example, leaves of Azalea plants exposed to 60 ppm·hrs. NO_2 were found to contain 8845 ppm. NO_3 on a dry-weight basis; when the exposure value was doubled, plants of this species contained only

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[1] Phenoldisulfonic acid was prepared by dissolving 25 grams of pure phenol in 150 ml. of concentrated H_2SO_4, to which 75 ml. of fuming sulfuric acid was added. The mixture was heated in a boiling water bath for two hours.

4885 ppm. Oleander plants responded in a different manner; when the exposure value was increased by a factor of 2, from 60 to 120 ppm·hrs, the foliar NO_3 content increased more than ten-fold, from 3899 to 44,115 ppm. Analyses of leaves of Hibiscus plants exposed to 60, 120, and 150 ppm·hrs. NO_2 showed the NO_3 content to be 1661, 12,453, and 6751 ppm, respectively.

Inherent biological variability and dissimilar sampling techniques cannot account for the extreme variability observed. The nutritional status of the experimental material with respect to nitrogen is probably the major cause. Although uniform cultural practices were provided at the test site, there is no way of determining the plants' status prior to delivery. It is concluded, therefore, that analysis of plant tissues as a basis for determining the amount of NO_2 polution is not practical.

5.0 EFFECTS OF HF AND NO_2 VAPOR ON SELECTED CITRUS AND ORNAMENTAL PLANTS

5.1 INTRODUCTION

The final series of fumigations were designed to determine the nature and extent of plant damage that might be expected in the event of an accidental release of toxic propellant during launch operations resulting in HF or NO_2 contaminated atmosphere.

Six different citrus varieties of economic importance, commercially grown in and around the Merritt Island Launch Area, were selected for the Phase III fumigations:

Hamlin Orange
Valencia Orange
Temple Orange
Pineapple Orange
Tangelo Orange
Marsh Seedless Grapefruit

Two ornamental species from each of the propellant sensitivity categories were selected from the 16 varieties screened in Phase II. Although the same species were used for both HF and NO_2 fumigations, the sensitivity ratings were not necessarily the same for the two pollutants (Table 4).

Exposures to HF were based on the results obtained from Phase II experiments. A range of exposure values was selected which would range from levels that would induce little or no damage to sensitive species up to the level which would cause injury to the more resistant species. Concentrations and times were selected so that two or more different concentrations and times of exposure resulted in the same total exposure values when expressed as ppm·hrs. In this way, the existence of reciprocity between these two parameters, as they affect plant injury, could be determined. The 15 HF and 13 NO_2 Phase III fumigations are described in Table 5.

Post-fumigation observations of all plants were made to assess the nature and extent of the pollutant-induced chlosoris, necrosis, defoliation, and flower and fruit abscission. In addition to these observations, all plants

TABLE 4

ORNAMENTAL SPECIES SELECTED FOR PHASE III FUMIGATIONS WITH HF AND NO_2, GROUPED ACCORDING TO THEIR RELATIVE SENSITIVITY TO THE POLLUTANTS AS DETERMINED IN PHASE II EXPERIMENTS

RELATIVE SENSITIVITY	POLLUTANT	
	HF	NO_2
Very sensitive	Azalea Hibiscus	Azalea Melaleuca
Moderately sensitive	Melaleuca Ixora	Hibiscus Ixora
Relatively resistant	Croton Carissa	Croton Carissa

TABLE 5

CONCENTRATION, DURATION AND TOTAL EXPOSURE FOR PHASE III PLANT FUMIGATIONS WITH HF AND NO_2

POLLUTANT	CONCENTRATION (ppm)	DURATION (hrs)	EXPOSURE (ppm·hrs)
HF	0.5	2	1
	0.5	4	2
	0.5	8	4
	1	2	2
	1	4	4
	1	8	8
	2	1	2
	2	2	4
	2	4	8
	4	1	4
	4	4	16
	4	8	32
	8	0.5	4
	8	1	8
	8	4	32
NO_2	25	4	100
	25	8	200
	50	2	100
	50	4	200
	50	8	400
	100	0.5	50
	100	1	100
	100	2	200
	150	2	300
	150	4	600
	200	0.5	100
	200	1	200
	250	1	250

were photographed before exposure to the pollutants and again at four and 14 days after fumigation. A selection of these photographs is included in Technical Volume 2 of this report. Technical Volumes 1 and 2, comprising the photographic recordings of plant injury and the laboratory manual covering methods for analysis of fluoride in plant tissue are not provided the same distribution as this report.

5.2 HYDROGEN FLUORIDE

5.2.1 POST-FUMIGATION OBSERVATIONS

5.2.1.1 Citrus Varieties

The six citrus varieties tested were all susceptible to HF, and the general pattern and progression of visible symptoms of injury were similar for all varieties; however, varietal differences in the extent and severity of HF-induced damage were obvious. The varieties are listed below in order of decreasing sensitivity to HF:

Marsh Seedless Grapefruit
Pineapple Orange
Temple Orange
Tangelo Orange
Hamlin Orange
Valencia Orange

The physiological age of citrus leaves affected their sensitivity to HF. For the purposes of this discussions, citrus leaves are divided into three age groups: (a) expanding young leaves (i.e., those arising from nodes at or near the terminal buds); (b) expanded young leaves (i.e., leaves produced during the current growing season but having attained full size); and (c) old leaves (i.e., leaves produced during the previous growing season).

To facilitate the description of HF-induced injury to citrus trees, the damage observed on relatively mild, moderate and severe exposures will be described in general terms. Summaries of post-fumigation observations of each citrus variety for each of the 15 Phase III HF fumigations are presented in Tables 6 through 11.

TABLE 6 SUMMARY OF VISIBLE RESPONSES OF MARSH SEEDLESS GRAPEFRUIT TO 15 HF CONCENTRATION x DURATION EXPOSURES

DURATION (Hours)	F CONCENTRATION (ppm) 0.5	1.0	2.0	4.0	8.0
0.5					50% defoliation of young leaves; remaining young leaves show severe tip necrosis. Occasional tip necrosis on old leaves.
1.0			Defoliation of 50% of young leaves; Tip necrosis on those remaining. No injury to old leaves.	60% defoliation of young leaves. Tip and marginal necrosis on most remaining young leaves, and occasionally on old leaves.	60% defoliation of young leaves with the remainder showing tip and marginal necrosis. Slight tip necrosis on old leaves.
2.0	60% defoliation of young leaves; Severe chlorosis or necrosis on those remaining. Excessive fruit abscission.	70% defoliation of young leaves; some cupping and necrosis on old leaves. Severe fruit abscission.	80% defoliation of young leaves; tip and marginal necrosis of remaining young leaves.		
4.0	75% defoliation of young leaves; remaining young leaves show chlorosis, tip necrosis, cupping and distortion. 100% fruit abscission.	80% defoliation of young leaves; remainder show tip and marginal necrosis. Occasional slight marginal necrosis on old leaves.	90% defoliation of young leaves; those remaining show severe necrosis on 50% of leaf surface. Tip necrosis on many old leaves.	100% defoliation of young leaves with tip and occasional marginal necrosis on some old leaves.	100% defoliation of young leaves; tip and marginal necrosis on some old leaves. 100% fruit abscission.
8.0	100% defoliation of young leaves; tip and marginal necrosis on old leaves. 100% fruit abscission.	100% defoliation of young leaves. Some succulent shoots and most old leaves necrotic. 100% fruit abscission.		100% defoliation of young leaves and considerable defoliation of old leaves. Severe marginal and tip necrosis throughout. Overall injury severe.	

TABLE 7 SUMMARY OF VISIBLE RESPONSES OF PINEAPPLE ORANGE TO 15 HF CONCENTRATION x DURATION EXPOSURES

DURATION (Hours)	F CONCENTRATION (ppm)				
	0.5	1.0	2.0	4.0	8.0
0.5					Tip and marginal necrosis covering 1-10% of leaf surfaces of most young leaves. Slight tip necrosis on old leaves.
1.0			30% defoliation of young leaves; tip necrosis on those remaining. Old leaves not injured.	60% defoliation of young leaves; remainder show slight tip necrosis. Old leaves not injured.	Defoliation of 80% of young leaves. Tip and marginal necrosis covering up to 10% of the surface of remaining young leaves.
2.0	10% defoliation of young leaves; remaining young leaves show moderate chlorosis and mild necrosis. Abscission of all fruit.	Defoliation of 25% of young leaves; moderate tip necrosis and severe marginal and intercostal chlorosis on remaining young leaves. 100% fruit drop.	60% defoliation of young leaves; 80% of those remaining show tip and occasional marginal necrosis.		
4.0	25% defoliation of young leaves; remaining young leaves show severe chlorosis, significant tip necrosis, cupping and distortion.	75% defoliation of young leaves; remaining young leaves show moderate tip and marginal necrosis with some young shoots necrotic.	Severe defoliation (up to 100%) and 10% of young shoots necrotic. Remaining leaves show moderate tip and slight marginal necrosis.	100% defoliation of young leaves and many succulent terminal shoots severely necrotic. Some slight tip necrosis on old leaves.	100% defoliation of young leaves; most young shoots necrotic. 5% of old leaves show slight tip and marginal necrosis. Overall damage severe.
8.0	Defoliation of 50% of young leaves; some necrosis on remaining fully expanded young leaves. Abscission of all fruit.			100% defoliation of young leaves; necrotic areas on fruit that did not drop. Tip necrosis on older foliage. Overall damage severe.	

TABLE 8 SUMMARY OF VISIBLE RESPONSES OF TEMPLE ORANGE TO 15 HF CONCENTRATION x DURATION EXPOSURES

DURATION (Hours)	F CONCENTRATION (ppm) 0.5	1.0	2.0	4.0	8.0
0.5					Defoliation of young leaves up to 10%. Slight to moderate tip necrosis of most young leaves. Old leaves not affected.
1.0			50% of young leaves show slight tip necrosis. Old leaves not affected.	Slight defoliation of young leaves and slight tip necrosis on 80% of young leaves. No damage to old leaves.	20% defoliation of young leaves; 50% of those remaining show slight tip necrosis. Old leaves not affected.
2.0	10-25% defoliation and occasional mild chlorosis on young leaves. No fruit abscission. Old leaves not affected.	Defoliation of up to 40% and severe chlorosis and occasional tip necrosis on young leaves. Moderate fruit abscission. Old leaves not affected.	Defoliation of 30-50% of young leaves. Slight tip and marginal necrosis of 10% of remaining young leaves. Old leaves not affected.		
4.0	Defoliation of up to 25% of young leaves. Tip and marginal necrosis on 50% of remaining leaves with moderate chlorosis and cupping. 100% fruit abscission. Old leaves not affected.	30% defoliation of young leaves and tip necrosis on 30% of the remaining young leaves. Old leaves not affected.	50% defoliation and tip and marginal necrosis on 50% of the remaining young leaves. Old leaves not affected.	Defoliation of 70% of young leaves. Remaining young leaves show tip and marginal necrosis with some in-rolled margins. Severe fruit drop. Old leaves not affected.	90% defoliation of young leaves and some young succulent shoots necrotic. 10-30% necrosis on remaining young leaves. Old leaves not affected.
8.0	Severe defoliation of young leaves (60-80%); remaining young leaves show necrosis and some chlorosis. 70% fruit abscission. Old leaves not affected.	80% defoliation of young leaves and moderate to severe necrosis on remaining young leaves. Old leaves not affected.		Defoliation of young leaves up to 100%. Severe tip and marginal necrosis on remaining young leaves. Some terminal shoots necrotic. Old leaves not affected.	

TABLE 9 SUMMARY OF VISIBLE RESPONSES OF TANGELO ORANGE TO 15 HF CONCENTRATION x DURATION EXPOSURES

DURATION (Hours)	F CONCENTRATION (ppm)				
	0.5	1.0	2.0	4.0	8.0
0.5					Slight tip necrosis of young leaves. Old foliage not affected.
1.0			25% defoliation of young leaves; some remaining young leaves show tip necrosis. Old leaves not injured.	30% defoliation of young leaves; slight tip necrosis on 50% of remaining young leaves.	30-50% defoliation of young leaves; slight tip necrosis on remaining young leaves.
2.0	10% of young leaves defoliated; moderate to severe chlorosis of remaining young leaves with occasional tip necrosis and cupping. Abscission of most fruit.	70% defoliation of young leaves; severe chlorosis of remaining young leaves with occasional tip necrosis. 100% fruit abscission.	Defoliation of 80% of young leaves with very slight tip necrosis on most of those remaining.		
4.0	70% defoliation of young leaves; many remaining young leaves severely chlorotic with some necrosis, cupping and other distortions. 100% fruit abscission.	90% defoliation of young leaves with the remainder showing tip and marginal necrosis. Old foliage not injured.	90% defoliation of young leaves; slight to moderate necrosis on those remaining.	100% defoliation of young leaves and excessive abscission of fruit.	100% defoliation of young leaves; young shoots severely necrotic. Abscission of all fruit.
8.0	80% defoliation of young leaves; remaining young leaves show distortions and tip and marginal necrosis. 100% fruit abscission.	100% defoliation of young leaves; tip necrosis on some old leaves.		100% defoliation of young leaves; mild to moderate tip necrosis on old leaves. Severe fruit abscission.	

TABLE 10 SUMMARY OF VISIBLE RESPONSES OF HAMLIN ORANGE TO 15 HF CONCENTRATION x DURATION EXPOSURES

DURATION (Hours)	F CONCENTRATION (ppm)				
	0.5	1.0	2.0	4.0	8.0
0.5					Tip or tip and marginal necrosis on most leaves, usually no more than 1 cm. of leaf tip necrotic; some necrotic areas along the margins of some leaves.
1.0			Defoliation of 5% of young leaves; 10% of remaining young leaves show slight tip necrosis. Old leaves not affected.	Some slight defoliation of young leaves; tip necrosis on 90% of young leaves; 5% show marginal necrosis covering up to 30% of leaf surface. Old leaves not affected.	5-10% defoliation of young leaves; remaining 95% show tip necrosis covering more than 1% of leaf surface. Slight marginal necrosis on 5% of the leaves. Old leaves show no effects.
2.0	10% defoliation of young leaves; mild chlorosis of remaining leaves. No evidence of fruit abscission.	20% defoliation of young leaves and abscission of all fruit. Tip necrosis in youngest leaves and severe chlorosis of young fully expanded leaves.	Defoliation of 20% of young leaves; 50% of remaining young leaves show slight tip and marginal necrosis.		
4.0	20% defoliation of young leaves. Most remaining leaves show tip necrosis and moderate to severe chlorosis. Many young leaves distorted; 100% fruit abscission.	20% defoliation and tip or tip and marginal necrosis of young leaves. No visible effects on old leaves.	20-30% defoliation and severe fruit abscission. Tip necrosis and marginal chlorosis common on young leaves. No damage to old leaves.	Defoliation of 50% of young fully expanded leaves. Severe (80-100%) fruit abscission. Old leaves not affected.	80% defoliation of young leaves and 100% fruit abscission. Remaining young leaves show tip and marginal necrosis on 1-10% of leaf surfaces.
8.0	Defoliation of 30% of young leaves; some marginal and tip necrosis. Old leaves appear normal.	80% defoliation of young leaves; remaining leaves show tip and marginal necrosis. Youngest expanding leaves show 100% necrosis. Succulent tips of some shoots also necrotic.		Defoliation of most young leaves (80-90%); tip and marginal necrotic areas on remaining leaves. Older leaves not affected.	

TABLE 11 SUMMARY OF VISIBLE RESPONSES OF VALENCIA ORANGE TO 15 CONCENTRATION x DURATION EXPOSURES

DURATION (Hours)	F CONCENTRATION (μpm) 0.5	1.0	2.0	4.0	8.0
0.5					Slight marginal and tip necrosis of most young leaves; some mild intercostal tissue collapse.
1.0			Slight defoliation (5%) of young leaves and some tip necrosis on remaining young leaves. No symptoms on old leaves.	5-10% defoliation of young leaves with tip and marginal necrosis covering up to 25% of leaf surface on 5% of remaining young leaves. No symptoms on old leaves.	25% defoliation of young leaves. Moderate to severe marginal necrosis up to 25% of leaf surface and slight tip necrosis on young leaves. Old leaves not injured.
2.0	10% defoliation of young leaves; remaining young leaves show moderate to severe chlorosis and occasional necrosis. Some foliar cupping evident. Old leaves not damaged.	Slight defoliation of young leaves (5-10%) and complete fruit abscission. 80-90% of young leaves show distortion or cupping. Old leaves not damaged.	20% defoliation of young leaves and tip necrosis on 80% of those remaining. Less than 1% show slight marginal necrosis as well. Old leaves not affected.		
4.0	25% defoliation of young leaves; considerable necrosis and severe chlorosis of remaining young leaves. Abscission of all fruits. Old leaves not affected.	Defoliation of 30% of young leaves; 50% of remaining young leaves show tip and marginal necrosis. Old leaves not affected.	Defoliation of at least 50% of young leaves; those remaining show tip and marginal necrosis covering up to 10% of leaf surface.	60% defoliation of young leaves. Old leaves not affected.	Defoliation of 80% of young leaves and abscission of all fruit. Tip and marginal necrosis on remaining young leaves. Old leaves normal.
8.0	Defoliation of 40% of young leaves. Tip and marginal necrosis and some intercostal chlorosis on remaining young leaves. Old leaves not damaged.	Complete necrosis of immature expanding leaves. 40% defoliation of young leaves. Remaining young leaves show moderate to severe tip and marginal necrosis. Old leaves not damaged.		80-90% defoliation of young leaves and severe tip and marginal necrosis of remaining leaves. No symptoms on old leaves.	

General chlorosis of expanding young leaves, which was more pronounced toward leaf tip, and chlorosis localized at the tip and along the margins of expanded leaves were the first obvious symptoms of relatively mild HF exposures. When the HF concentration was increased or the exposure time extended, wilting, marginal tissue collapse, or saturation of intercellular spaces with water were apparent within a relatively short time after fumigations. These damaged areas usually become necrotic. Occasional damage of intercostal leaf tissues and defoliation of young leaves also was noticed.

Fumigations with relatively high exposures of HF induced excessive abscission of young leaves and developing fruits. When young leaves abscissed, separation usually occurred at the base of the leaf blade, leaving the petioles in tact. Older leaves defoliated in the normal manner, at the base of the petiole. Defoliation usually occurred after visible symptoms of injury were evident; however, in many cases young leaves that showed no symptoms of injury abscissed.

Leaves on plants subjected to relatively high HF exposures which did not abscisse, displayed symptoms of severe tip, marginal and intercostal necrosis, as well as cupping and other distortions. Necrosis and wilting of succulent portions of elongating shoots were also observed.

5.2.1.2 Ornamental Species

Description of the post-fumigation conditions of the six ornamental species for each of the 15 Phase III fumigations are presented in Tables 12 through 17. The general responses of each specie to HF fumigation are listed below:

Azalea: Azalea was one of the most HF-sensitive species in these experiments. The lowest concentration x duration (0.5 ppm for two hours) resulted in necrotic areas on ten to forty percent of the surface of all young expanding leaves. Occasional necrosis was observed on older leaves also. HF exposure at 1 ppm for four hours resulted in moderate to severe defoliation and severe tip and marginal necrosis of remaining leaves. Exposures providing eight or more ppm·hrs, were extremely phytotoxic.

Carissa: Plants of this specie were relatively insensitive to HF exposure. The two highest exposures (4 ppm for eight hours and 8 ppm for four hours) were the only fumigations in which visible symptoms of HF injury were

induced. The observed injury was limited to slight tip necrosis and intercostal necrotic spotting on young expanding leaves. No defoliation occurred. All other concentration x duration exposures were without effect.

Croton: The variegated pigment pattern of Croton foliage made evaluation of visible injury difficult. Critical inspection of these plants revealed some minor tip and marginal necrosis on expanding leaves of plants exposed to the highest dosages of HF (32 ppm·hrs). Following exposure to 8 or 16 ppm·hrs, no leaf markings were evident, but appreciable defoliation of older leaves was observed. Croton plants receiving lower levels of HF were not visibly affected.

Hibiscus: All exposures to HF induced foliar injury on Hibiscus plants. Injury ranged from mild chlorosis induced by low dosages to severe necrosis on 80 percent of the leaves of all ages at the higher levels. Defoliation was not readily induced. Leaves that were killed often remained attached to the plant for more than one week. Regrowth from severely injured plants appeared normal.

Ixora: Exposures to 1, 2, and 4 ppm·hrs did not materially affect Ixora plants. When fumigated for eight hours with HF at 1 ppm, severe marginal and tip necrosis was observed on 75 percent of the young and middle-aged leaves, which would defoliate readily when touched. Older foliage showed only slight necrotic spotting. The reverse concentration x duration exposure (8 ppm for one hour) induced only slight marginal necrosis.

Melaleuca: Complete necrosis of Melaleuca foliage occurred within seven days after the mildest Phase III fumigation (0.5 ppm for two hours). All other concentration x duration exposures were equally phytotoxic.

HF was not lethal to any of the plants fumigated in Phase III. Regrowth of axillary buds was observed on all plants within three to six weeks after fumigation.

TABLE 12 SUMMARY OF VISIBLE RESPONSES OF AZALEA TO 15 HF CONCENTRATION x DURATION EXPOSURES

DURATION (Hours)	F CONCENTRATION (ppm) 0.5	1.0	2.0	4.0	8.0
0.5					Tip and marginal chlorosis on 30% of the leaves. 10% of leaf area of expanded leaves and 50% of expanding leaves affected.
1.0			Isolated necrotic spots on 5% of the leaves covering no more than 10% of leaf surface.	Necrotic areas on 50% of the leaves covering 10-50% of leaf surface; tip and marginal as well as general necrosis present.	Necrosis on 40% of the leaves ranging from slight tip burn to 30% of leaf surface.
2.0	Necrosis on 10-60% of leaf surface of expanding and fully expanded young leaves. Occasional necrosis on older leaves.	Necrosis of 5-30% of leaf surface of young expanding leaves. Some necrosis on older leaves showing no specific pattern.	Slight to moderate tip necrosis covering up to 20% of leaf surface of young leaves. Less than 1% of older leaves necrotic.		
4.0	10-30% necrosis of youngest and expanding leaves; occasional necrosis on older foliage.	60% of the leaves necrotic on 10-40% of leaf surface; both tip and marginal necrosis.	Necrosis of 90% of young leaves covering up to 60% of leaf surface. Leaves at lowest whorls show no effect.	All young leaves severely necrotic and defoliate readily when disturbed. Older foliage moderately necrotic.	100% of young leaves and shoots severely necrotic. Older leaves show necrotic spotting covering 10-80% of leaf surface.
8.0	Severe tip necrosis of youngest leaves covering 10-50% of leaf surface.	Necrosis on 90% of all leaves, ranging from slight tip necrosis or a few spots on old leaves to 100% necrosis of young leaves.		Very severe damage. Moderate to severe defoliation; remaining leaves severely (80-100%) necrotic.	

TABLE 13 SUMMARY OF VISIBLE RESPONSES OF HIBISCUS TO 15 HF CONCENTRATION x DURATION EXPOSURES

DURATION (Hours)	F CONCENTRATION (ppm) 0.5	1.0	2.0	4.0	8.0
0.5					Intercostal tissue collapse and chlorosis of 40-50% of the leaves. No evidence of necrosis.
1.0			Some chlorosis along veins; no other effects.	Occasional slight tip and marginal necrosis.	Tip, marginal and intercostal necrosis.
2.0	Occasional mild intercostal necrosis of young leaves. Mild tip necrosis on 20% of young leaves.	Moderate necrosis of young expanding leaves, both tip and marginal.	Moderate necrosis and mild intercostal chlorosis on both young and old leaves.		
4.0	Moderate intercostal necrosis and some cupping of young leaves.	Tip, marginal and intercostal necrosis of young leaves.	Moderate tip and marginal necrosis on young leaves; less severe on old leaves.	Moderate to severe necrosis on 80% of leaves regardless of age.	Moderate marginal necrosis on old leaves; young foliage severely necrotic. Anthocyanosis on varigated variety.
8.0	Moderate marginal and intercostal necrosis of young leaves. Bracts of flower buds show tip necrosis. Some defoliation of old leaves.	80% of young leaves show tip and marginal necrosis covering up to 50% of leaf surface. Some intercostal necrosis on old leaves.		Moderate tip and marginal necrosis of older leaves. Young leaves severely necrotic. Anthocyanosis on varigated variety.	

TABLE 14 SUMMARY OF VISIBLE RESPONSES OF MELALEUCA TO 15 HF CONCENTRATION x DURATION EXPOSURES

DURATION (Hours)	F CONCENTRATION (ppm) 0.5	1.0	2.0	4.0	8.0
0.5					No visible injury.
1.0			No visible injury.	Tip necrosis on 25% of surface of young leaves. Occasional intercostal necrosis on older leaves.	Tip necrosis covering 30-50% of surface of terminal expanding leaves. Occasional tip necrosis on old leaves.
2.0	Slight tip necrosis and moderate intercostal necrosis of young leaves.	General necrosis of many young leaves. Slight defoliation of older leaves.	Young leaves show necrosis covering up to 50% of leaf surface. Some defoliation of older leaves.		
4.0	Severe necrosis of many leaves regardless of age.	Necrotic spotting on 80% of the old leaves; severe necrosis of young leaves. Moderate defoliation.	Severe necrosis of young and old leaves; moderate to severe defoliation. Slight necrosis on succulent shoots.	Severe tip necrosis and wilting of youngest leaves and stems. Severe intercostal necrosis on 40-100% of leaf surface of older leaves.	30% defoliation of young leaves; remaining young leaves show necrosis on 50-100% of leaf surface. Severe necrosis on lower shoots.
8.0	Severe necrosis and defoliation of most leaves. 50% of remaining leaves show complete necrosis.	Severe necrosis on young leaves and on many succulent shoots. Moderate defoliation.			

TABLE 15 SUMMARY OF VISIBLE RESPONSES OF IXORA TO 15 HF CONCENTRATION x DURATION EXPOSURES

DURATION (Hours)	F CONCENTRATION (ppm)				
	0.5	1.0	2.0	4.0	8.0
0.5					No visible injury.
1.0			No visible injury.	No visible injury.	No visible injury.
2.0	No visible injury.	No visible injury.	No visible injury.		
4.0	No visible injury.	No visible injury.	Occasional marginal necrosis covering a maximum of 20% of leaf surface.	100% of expanding young leaves show tip necrosis covering up to 75% of leaf surface. Fully expanded young leaves show moderate to severe marginal necrosis. Moderate defoliation.	10-25% defoliation; remaining leaves show tip and marginal necrosis (regardless of age).
8.0	Occasional slight tip necrosis on developing leaves.	Moderate to severe tip and marginal necrosis on 75% of expanding and fully expanded young leaves. These defoliate readily when disturbed.		Severe tip and marginal necrosis of most leaves. Moderate defoliation. Some young shoots necrotic.	

TABLE 16 SUMMARY OF VISIBLE RESPONSES OF CROTON TO 15 HF CONCENTRATION x DURATION EXPOSURES

DURATION (Hours)	F CONCENTRATION (ppm)				
	0.5	1.0	2.0	4.0	8.0
0.5					No visible injury.
1.0			No visible injury.	No visible injury.	No visible injury.
2.0	No visible injury.	No visible injury.	No visible injury.		
4.0	No visible injury.	No visible injury.	No visible injury.	No visible injury.	No visible injury.
8.0	Slight tip necrosis and slight defoliation of young leaves.	Slight tip necrosis of some expanding young leaves. Many leaves defoliate when disturbed.		Youngest expanding leaves show tip necrosis. Moderate defoliation of leaves of all ages.	

TABLE 17 SUMMARY OF VISIBLE RESPONSES OF CARISSA TO 15 HF CONCENTRATION x DURATION EXPOSURES

DURATION (Hours)	F CONCENTRATION (ppm) 0.5	1.0	2.0	4.0	8.0
0.5					No visible injury.
1.0			No visible injury.	No visible injury.	No visible injury.
2.0	No visible injury.	No visible injury.	No visible injury.		
4.0	No visible injury.	No visible injury.	No visible injury.	No visible injury.	Necrotic areas covering 30% of leaf surface on several leaves. Very limited occurance.
8.0	Tip necrosis covering up to 20% of surface of youngest expanding leaves.	Tip and marginal necrosis on terminal expanding leaves.			

5.2.2 TISSUE ANALYSIS

Fluoride will adsorb to surface tissues of plants exposed to HF. This surface fluoride is relatively non-toxic, but serves as a source of absorbed fluoride. In chronic (long duration, low concentrations) exposures of plants to HF, absorbed fluoride, which is extremely soluble in water, is readily transported to the terminal portion of the leaf via the transpirational stream where it accumulates. When a special concentration is attained in the leaf, tissue damage becomes evident. The first symptom of HF-induced plant injury, therefore, usually appears at the tip and margins of leaves. Since most of the absorbed fluoride is accumulated by leaves, foliar analyses for F are commonly used to verify visible symptoms when chronic HF pollution is suspected.

A part of this study was to confirm that analysis of F in tissue could be used to determine injury induced by relatively high concentrations of HF for short time periods. All plants subjected to HF fumigations were divided into eight sectors, representing each quadrant in upper and lower sectors. A total of eight to 16 leaves from the eight sectors constituted a sample for F analysis. The number of sampled leaves was purposely kept small to minimize damage due to defoliation and to allow for continual observation of the experimental plants.

Two samples were taken from each plant; one sample was washed in Alconox/EDTA solution and used to estimate absorbed (internal) fluoride content, and the other, which was not washed, served as an estimate of the total fluoride content (external plus internal). Leaf washing techniques as a method employed for fluorine analysis are described in detail in Technical Volume I of this report. Technical Volume I is not provided the same distribution as this report.

The average F content of the three washed and three unwashed leaf samples of the citrus varieties and ornamental species from each of the HF exposures are shown in Table 18. The correlation between the F content of washed and unwashed foliage samples was determined for the pooled data for the six citrus varieties and the six ornamental species and for each specie or variety individually (Table 19). In every case, there was a positive correlation between total F content (unwashed leaves) and the internal F concentration (washed leaves).

TABLE 18

MEAN FOLIAR FLUORINE CONTENT, IN PARTS PER MILLION (DRY WEIGHT) OF HF-FUMIGATED CITRUS AND ORNAMENTAL PLANTS
VALUES ARE PRESENTED FOR BOTH WASHED (UPPER NUMBER) AND UNWASHED (LOWER NUMBER) LEAVES

Fumigation No.	Exposure			Citrus Varieties						Ornamental Species					
	Concn. (ppm)	Time (hr)	Time x Concn.	Hamlin	Valencia	Temple	Pineapple	Tangelo	Marsh	Azalea	Carissa	Croton	Hibiscus	Ixora	Melaleuca
F-1	4	4	16	200.4 472.3	142.9 359.9	293.1 587.7	182.5 369.3	149.5 357.8	224.8 387.1	285.8 307.2	226.8 192.9	405.9 476.8	582.4 542.8	197.5 206.6	488.9 463.1
F-2	8	4	32	372.2 581.0	316.8 555.5	293.2 588.0	294.8 572.6	291.3 684.2	242.0 468.2	219.0 278.6	292.5 582.6	757.2 967.2	1162.6 1778.1	350.6 558.5	987.7 1322.2
F-3	4	8	32	394.9 536.9	388.0 378.9	389.2 519.0	400.4 532.3	350.4 590.0	453.3 623.9	567.2 753.2	356.8 456.8	710.4 1307.7	697.6 1022.6	211.2 470.1	578.8 723.3
F-4	4	1	4	195.0 284.6	140.9 265.7	150.3 182.9	70.6 103.9	117.4 153.5	177.8 299.0	90.6 165.8	120.8 164.2	240.3 370.5	163.6 391.1	81.3 175.0	141.7 252.4
F-5	2	4	8	187.9 287.1	204.8 294.8	244.8 361.7	224.3 377.4	245.9 300.8	225.8 298.6	185.8 397.9	165.6 244.8	405.8 586.9	557.9 896.5	142.4 243.7	261.2 387.1
F-6	2	2	4	86.9 161.5	94.6 209.3	124.4 262.8	102.4 207.6	52.4 153.2	68.4 157.4	46.8 127.5	103.6 158.8	171.4 254.6	264.2 335.6	138.6 227.6	233.8 394.4
F-7	2	1	2	56.0 87.1	24.6 57.0	29.3 68.5	35.8 66.5	19.7 52.9	12.4 29.7	26.0 38.2	24.0 64.4	35.0 69.8	72.3 140.2	44.7 35.4	84.3 95.4
F-8	1	4	4	55.4 183.2	93.5 203.5	63.0 140.1	74.4 176.4	106.1 299.2	110.9 235.8	77.0 190.0	117.6 188.5	135.6 322.5	113.6 264.2	121.2 179.7	145.9 227.6
F-9	8	1	8	105.3 255.3	132.5 192.7	84.8 185.3	121.9 241.8	66.3 205.2	149.3 216.0	92.3 162.1	109.7 182.4	197.3 297.1	208.4 322.7	165.7 196.7	180.4 261.8
F-10	8	0.5	4	109.7 137.9	114.0 184.8	59.2 145.2	54.1 107.9	70.2 149.4	99.3 113.9	62.9 151.7	66.0 128.4	140.4 259.5	95.8 282.4	134.0 171.9	117.1 195.3
F-11	1	8	8	124.6 274.7	124.3 309.0	110.8 241.0	92.7 238.9	118.0 279.8	99.2 283.2	91.9 302.7	112.4 265.2	181.4 526.2	178.4 404.1	133.7 321.2	318.1 333.3
F-12	0.5	8	4	75.7 141.7	59.0 137.3	80.0 153.9	95.3 153.2	82.2 203.4	82.1 127.9	81.4 136.4	72.3 89.2	144.5 221.5	195.1 247.9	98.3 84.5	191.3 164.5
F-13	0.5	4	2	45.0 70.9	48.3 75.6	50.6 85.4	47.2 70.8	57.7 65.9	62.5 67.3	14.3 46.5	67.0 79.8	187.4 230.8	111.3 145.3	105.5 98.7	101.9 118.0
F-14	0.5	2	1	16.8 57.2	22.6 38.6	21.2 42.9	19.1 44.8	*	*	9.4 57.5	30.7 45.3	44.8 65.0	58.2 115.7	31.7 84.3	28.9 31.7
F-15	1	2	2	36.8 103.3	27.2 75.9	35.9 57.9	27.5 55.8	27.3 40.2	21.7 64.2	15.8 48.2	18.4 79.7	68.7 143.1	33.6 232.1	51.3 110.4	72.6 129.9

*No valid estimate of fluorine content.

TABLE 19

LINEAR REGRESSIONS FOR MEAN VALUES OF FLUORIDE CONTENT OF UNWASHED AND WASHED LEAF TISSUE OF EACH SPECIES OR VARIETY OF HF-FUMIGATED PLANTS

TISSUE	REGRESSION EQUATION*	CORRELATION COEFFICIENT	NUMBER OF X,Y PAIRS
Citrus Varieties (pooled)	$\hat{Y} = 46.01 + 1.44x$	0.924	88
Hamlin Orange	$\hat{Y} = 52.80 + 1.38x$	0.943	15
Valencia Orange	$\hat{Y} = 71.53 + 1.17x$	0.867	15
Temple Orange	$\hat{Y} = 31.99 + 1.55x$	0.949	15
Pineapple Orange	$\hat{Y} = 37.12 + 1.50x$	0.957	15
Tangelo Orange	$\hat{Y} = 37.46 + 1.72x$	0.911	14
Marsh Grapefruit	$\hat{Y} = 40.08 + 1.38x$	0.947	14
Ornamental Species (pooled)	$\hat{Y} = 34.80 + 1.35x$	0.956	90
Azalea	$\hat{Y} = 57.56 + 1.18x$	0.960	15
Carissa	$\hat{Y} = 23.90 + 1.36x$	0.897	15
Croton	$\hat{Y} = 40.25 + 1.44x$	0.943	15
Hibiscus	$\hat{Y} = 66.61 + 1.36x$	0.965	15
Ixora	$\hat{Y} = -4.01 + 1.61x$	0.885	15
Melaleuca	$\hat{Y} = 11.95 + 1.25x$	0.978	15

* $\hat{Y} = a + bx$ where x = fluorine content of washed leaves
Y = fluorine content of unwashed leaves

The correlation between total and internal F of the pooled data for all citrus varieties and for all ornamental species are illustrated in Figures 1 and 2, respectively. The slope of the regression suggests that of the total F accumulated by citrus foliage, approximately 30 percent was surface-born (Figure 1). The pooled data for the six ornamental species indicated that about 25 percent of the total F accumulated was removed by washing (Figure 2). Thus, when all citrus varieties and all ornamental species are considered together over the wide range of concentration x duration exposures employed, approximately 70 percent of the total foliar fluoride accumulated by citrus leaves, and 75 percent accumulated by ornamental leaves, was within the leaf tissues.

The data of Table 18 were used to construct the Histograms in Figures 3 through 14 to facilitate comparisons of F accumulations in relation to exposure. The exposure values, at ppm·hrs, were arranged on the X axes such that two or more concentration x duration values resulting in the same exposure value could be readily compared.

Although there was a general reduction in the tissue F content with decreasing exposure value, the contribution of HF concentration or duration of exposure within a given exposure value was not necessarily consistent. For example, in the 8 ppm HF for one hour and the 1 ppm HF for 8 hours fumigations, the duration of exposure exerted a greater influence on the amount of F accumulated by most plants than did HF concentration. However, when fumigations providing 8 ppm HF for four hours and 4 ppm HF for eight hours were compared, the effect of concentration predominated. Over such a wide range of exposure values (1 to 32 ppm·hrs), the relative contribution of HF concentration and duration of fumigation cannot be separated.

5.3 NITROGEN TETROXIDE

5.3.1 Post-fumigation Observations

Due to the relatively high nitrogen content and the diverse nature of nitrogen-containing compounds in plant tissues, very little is known of the manner in which atmospheric NO_2 is absorbed, translocated, or of the way in which it damages plant tissues.

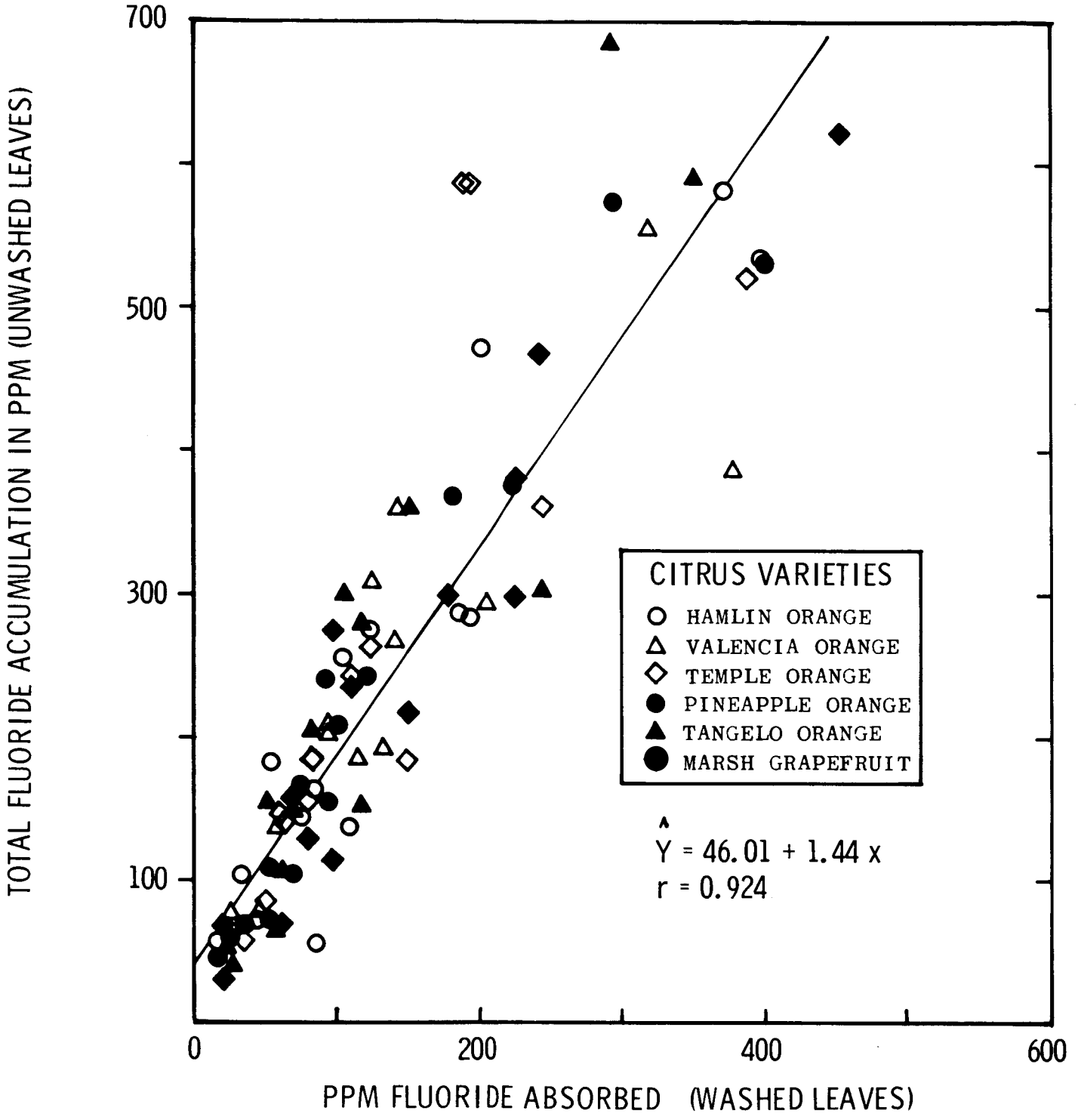

FIGURE 1 INTERNAL AND TOTAL FLUORIDE CORRELATION DATA (CITRUS)

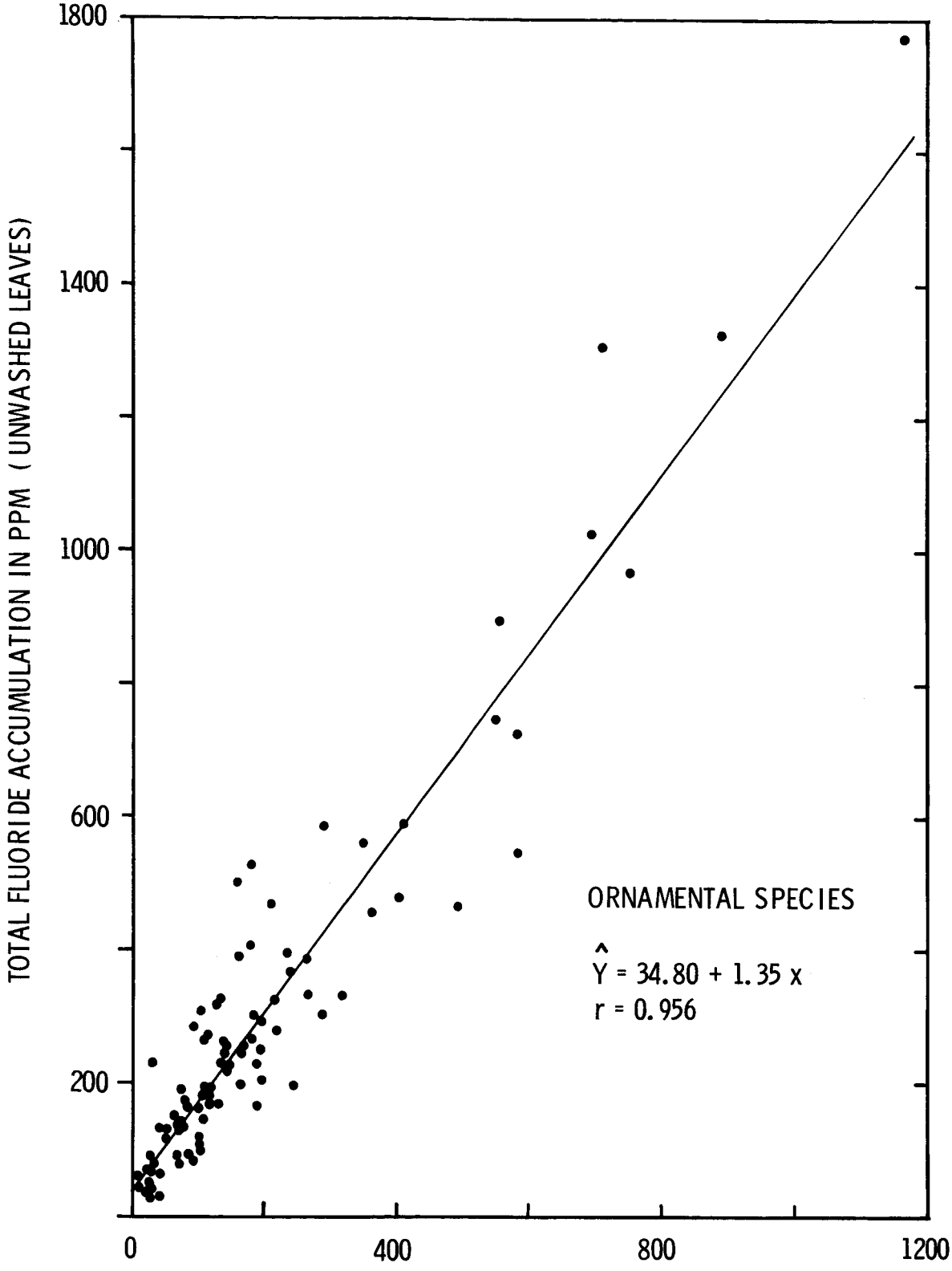

FIGURE 2 INTERNAL AND TOTAL FLUORIDE CORRELATION DATA (ORNAMENTAL)

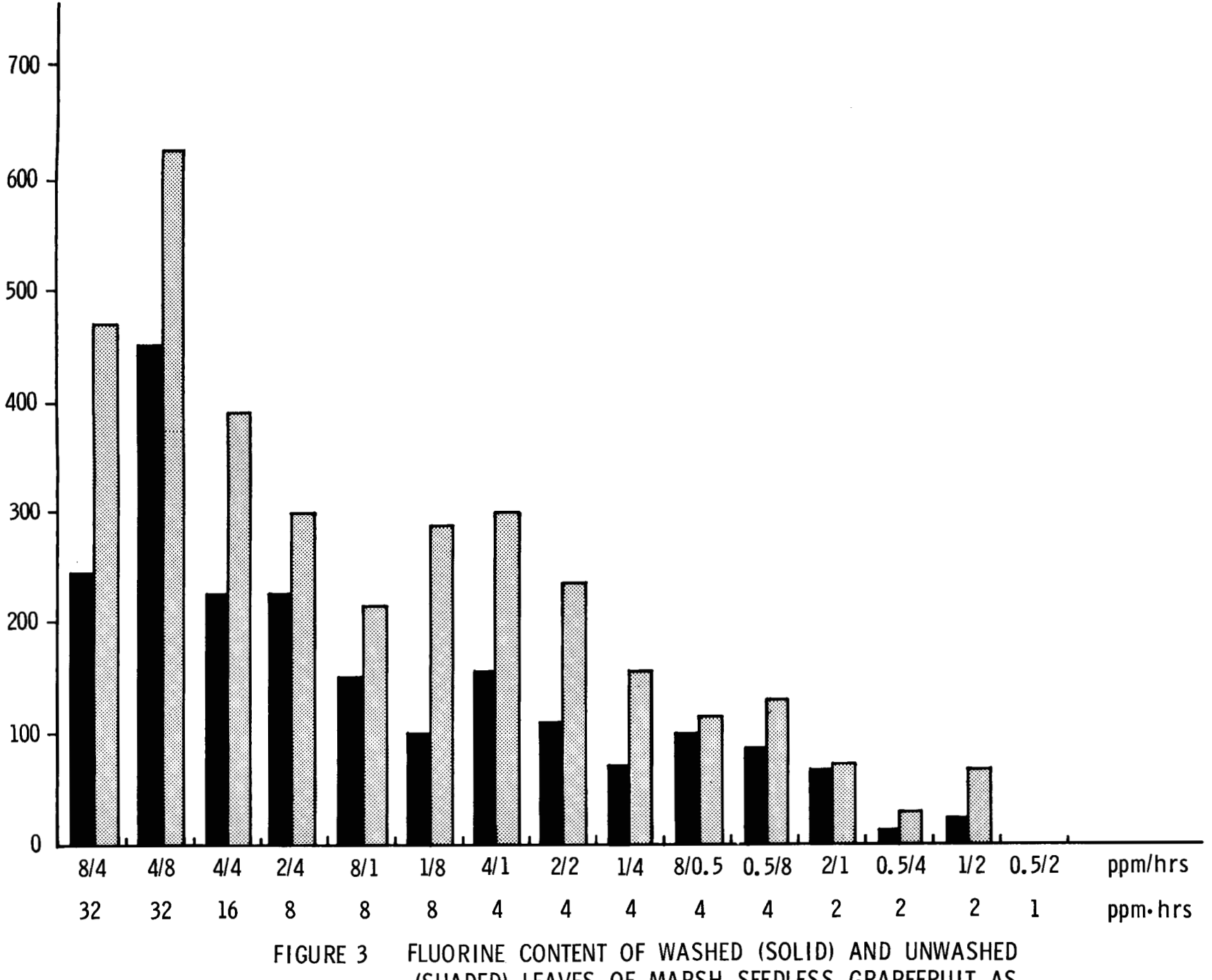

FIGURE 3 FLUORINE CONTENT OF WASHED (SOLID) AND UNWASHED (SHADED) LEAVES OF MARSH SEEDLESS GRAPEFRUIT AS AFFECTED BY EXPOSURE VALUE

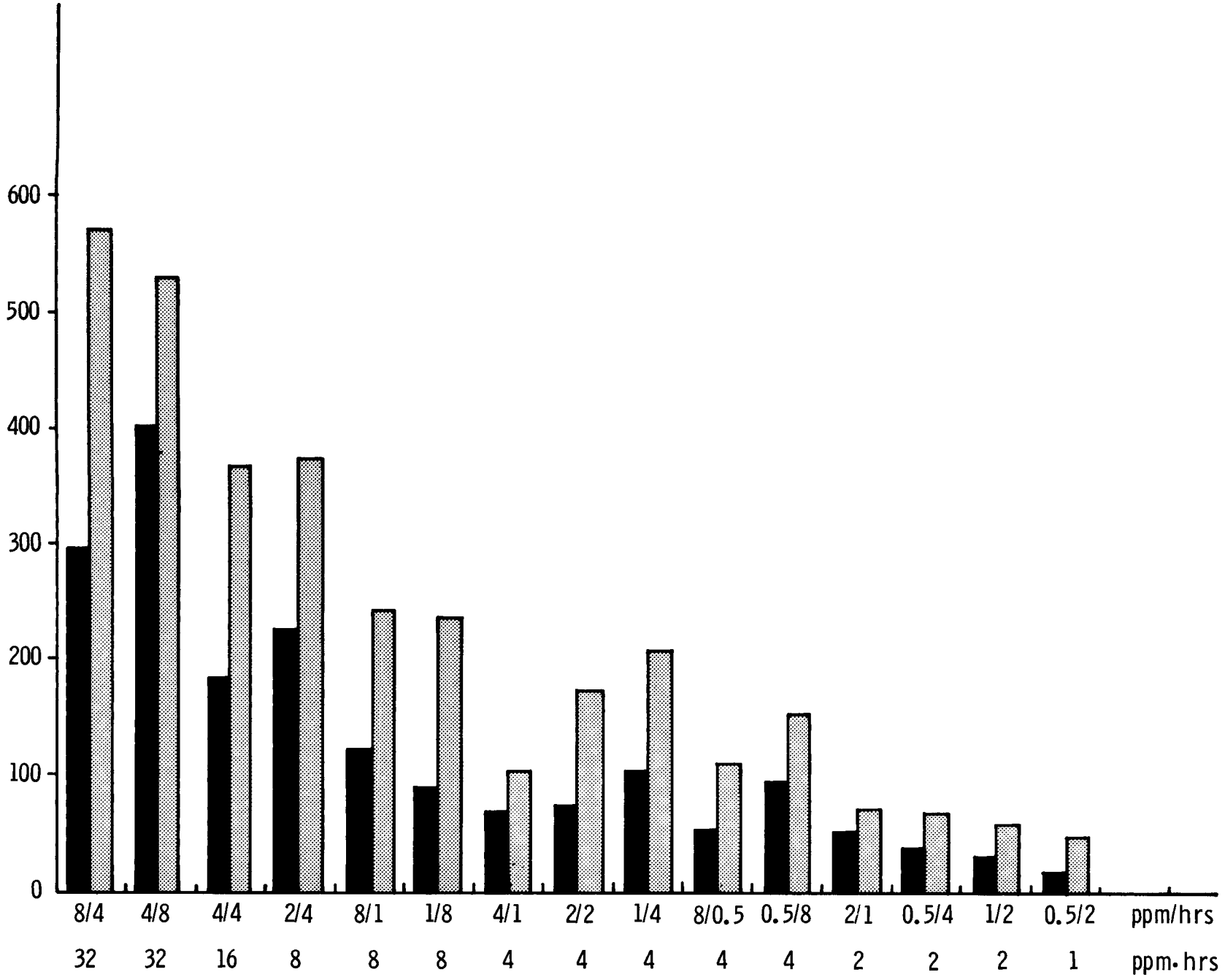

FIGURE 4 FLUORINE CONTENT OF WASHED (SOLID) AND UNWASHED (SHADED) LEAVES OF PINEAPPLE ORANGE AS AFFECTED BY EXPOSURE VALUE

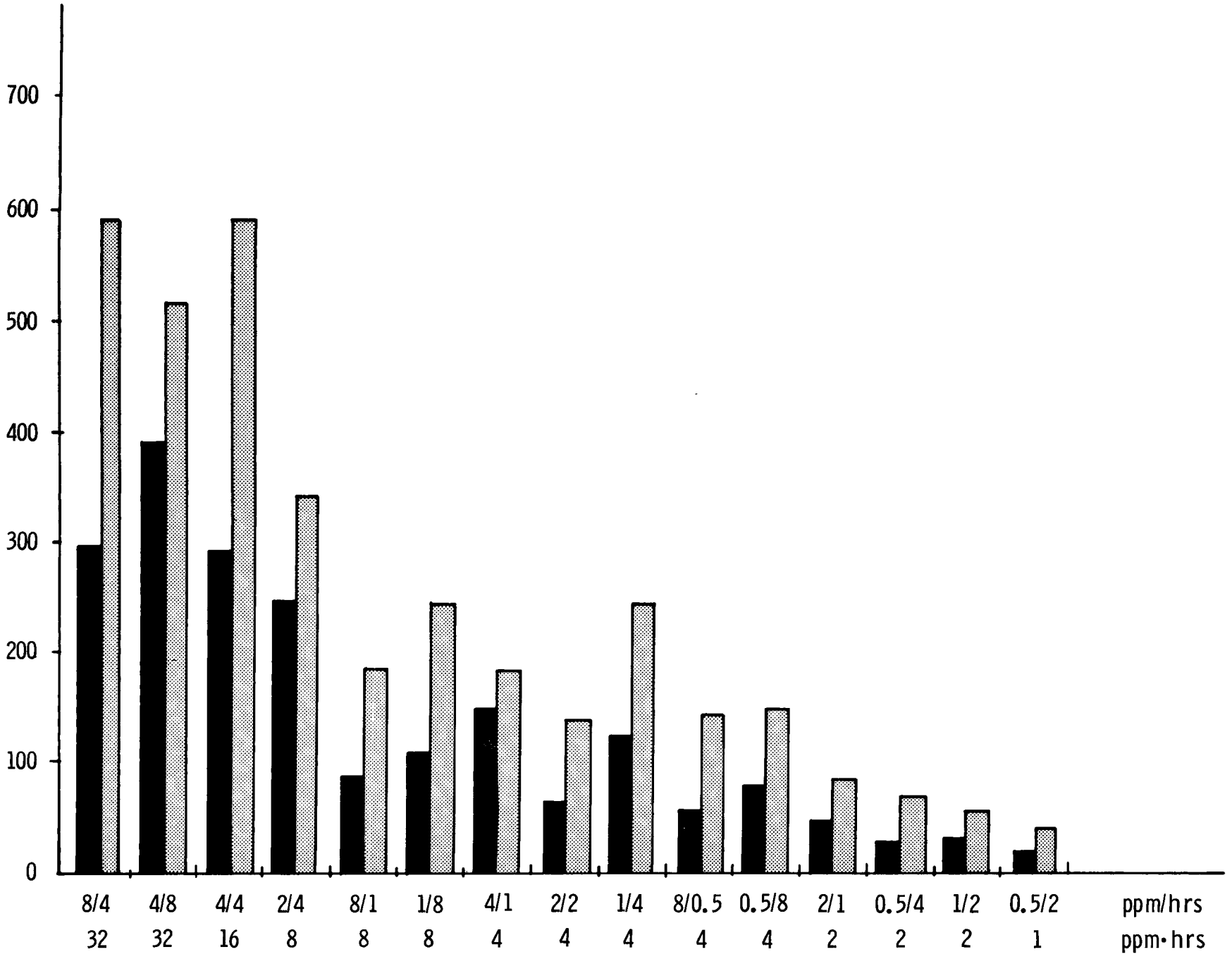

FIGURE 5 FLUORINE CONTENT OF WASHED (SOLID) AND UNWASHED (SHADED) LEAVES OF TEMPLE ORANGE AS AFFECTED BY EXPOSURE VALUE

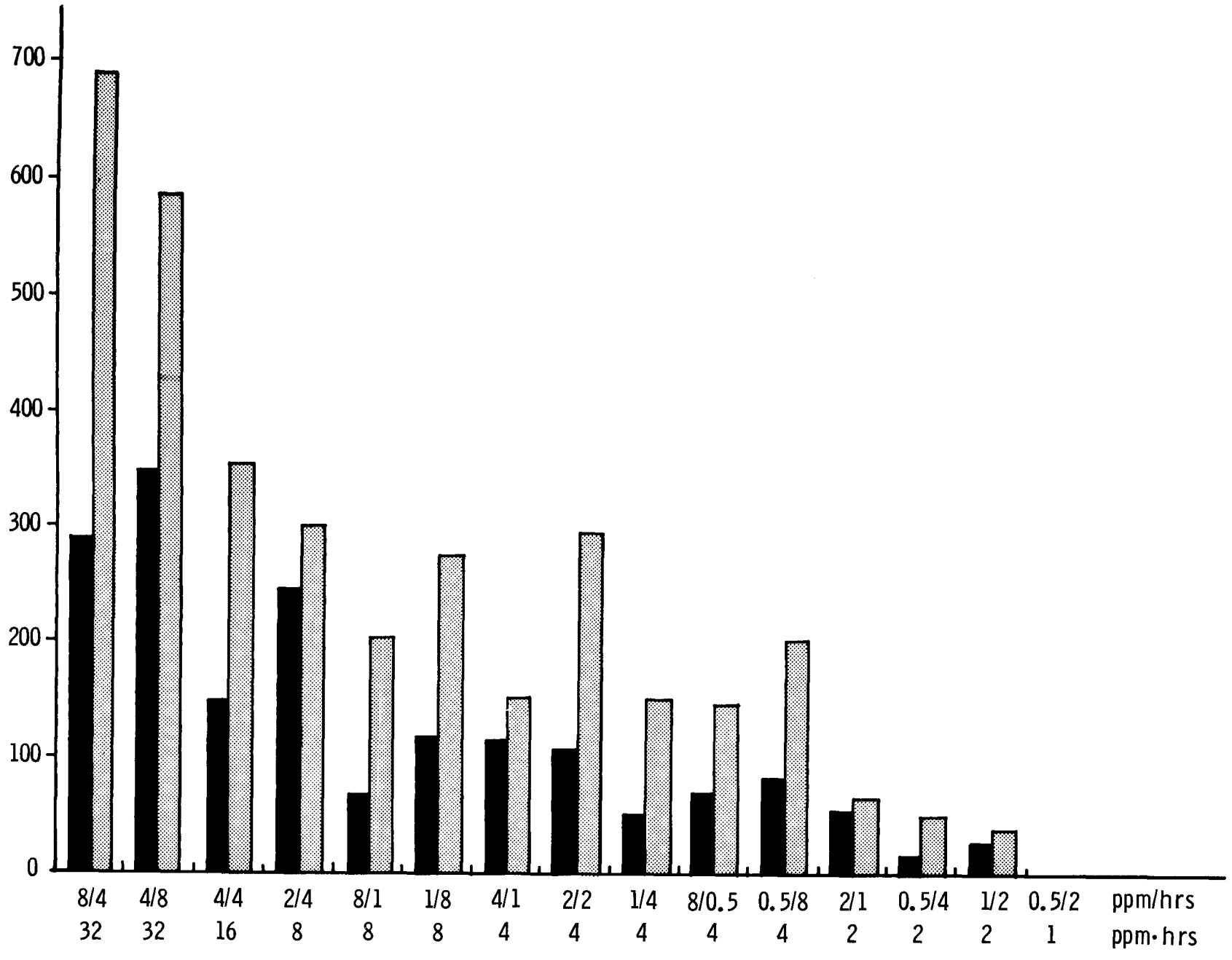

FIGURE 6 FLUORINE CONTENT OF WASHED (SOLID) AND UNWASHED (SHADED) LEAVES OF TANGELO ORANGE AS AFFECTED BY EXPOSURE VALUE

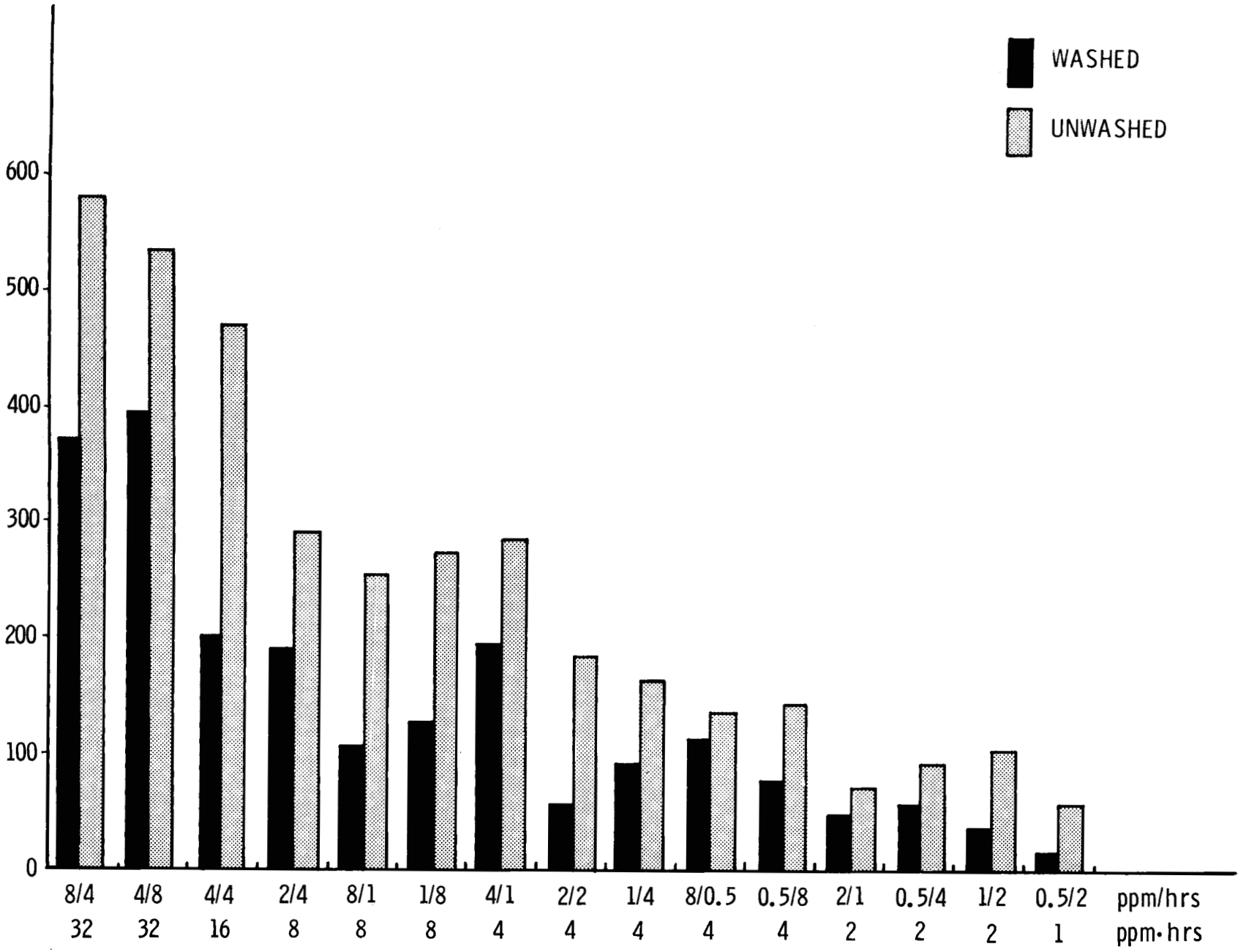

FIGURE 7 FLUORINE CONTENT OF WASHED (SOLID) AND UNWASHED (SHADED) LEAVES OF HAMLIN ORANGE AS AFFECTED BY EXPOSURE VALUE

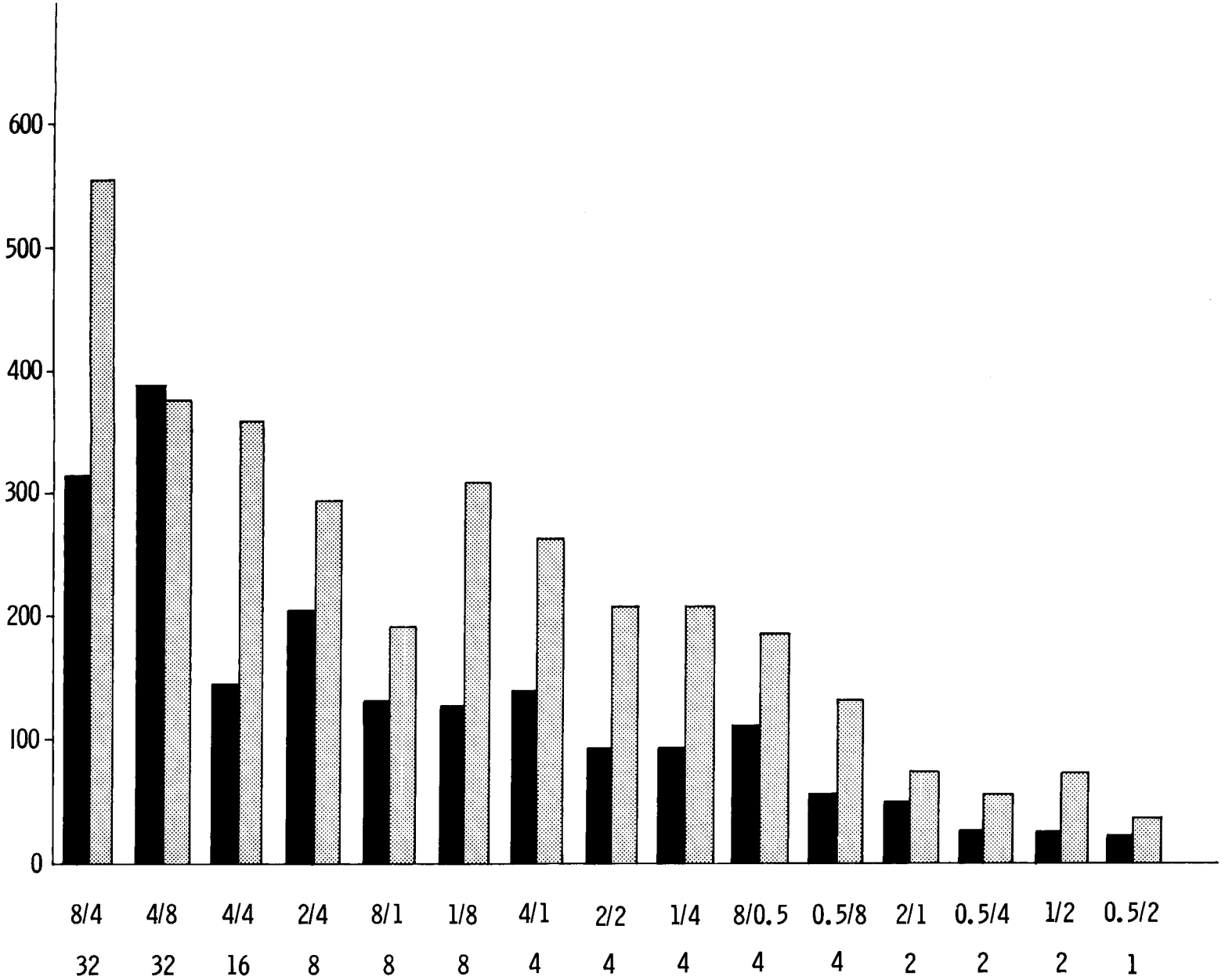

FIGURE 8 FLUORINE CONTENT OF WASHED (SOLID) AND UNWASHED (SHADED) LEAVES OF VALENCIA ORANGE AS AFFECTED BY EXPOSURE VALUE

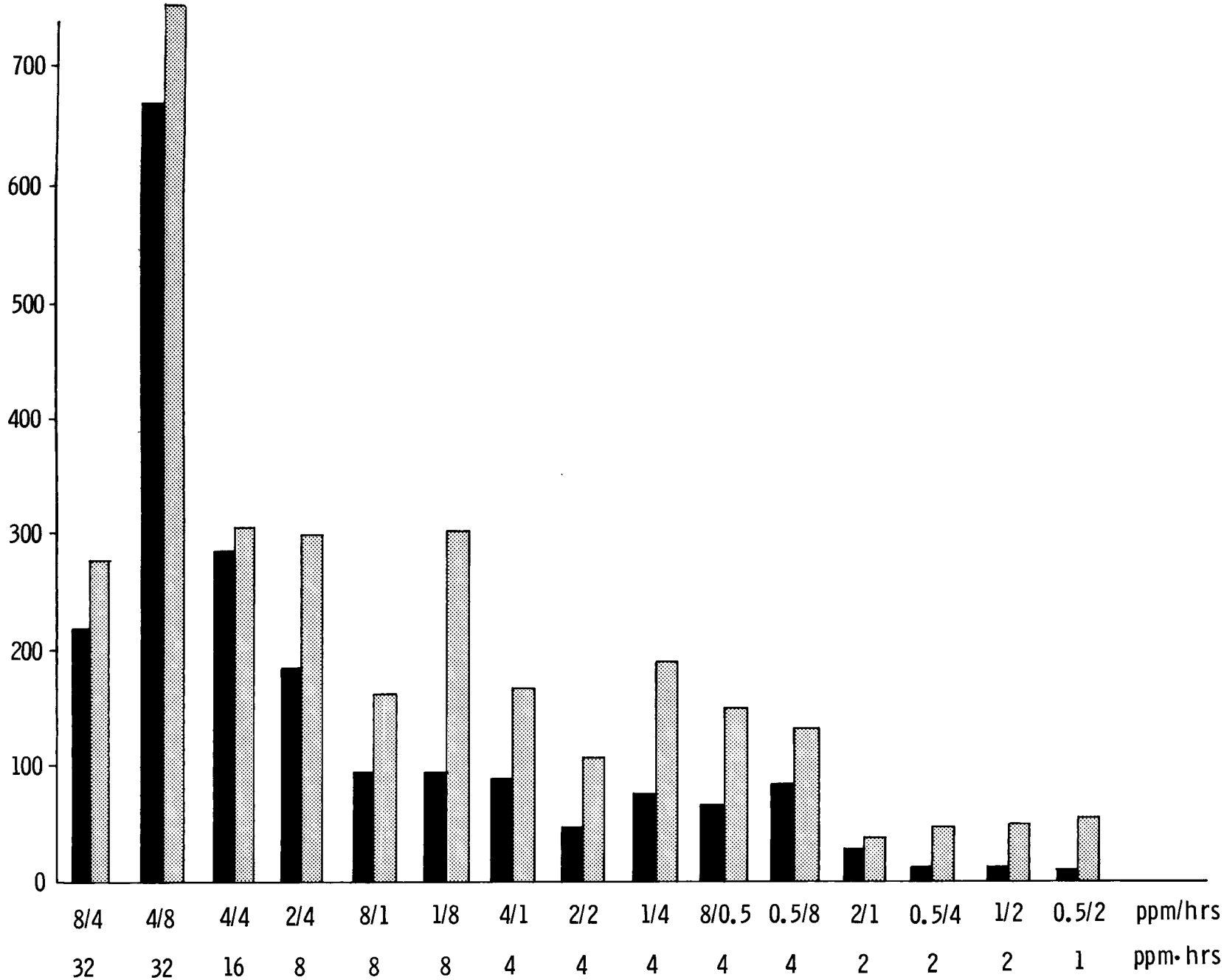

FIGURE 9 FLUORINE CONTENT OF WASHED (SOLID) AND UNWASHED (SHADED) LEAVES OF AZALEA AS AFFECTED BY EXPOSURE VALUE

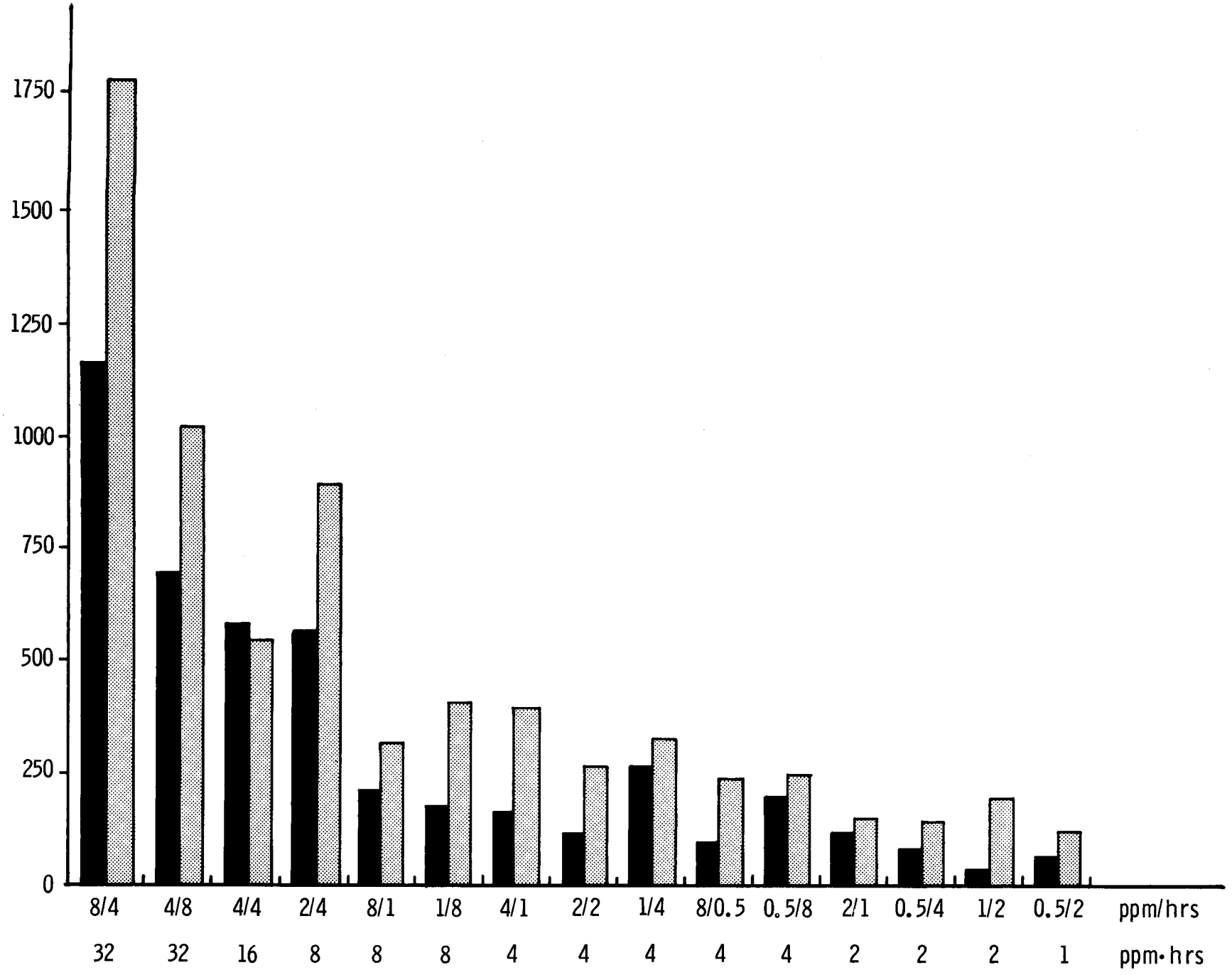

FIGURE 10 FLUORINE CONTENT OF WASHED (SOLID) AND UNWASHED (SHADED) LEAVES OF HIBISCUS AS AFFECTED BY EXPOSURE VALUE

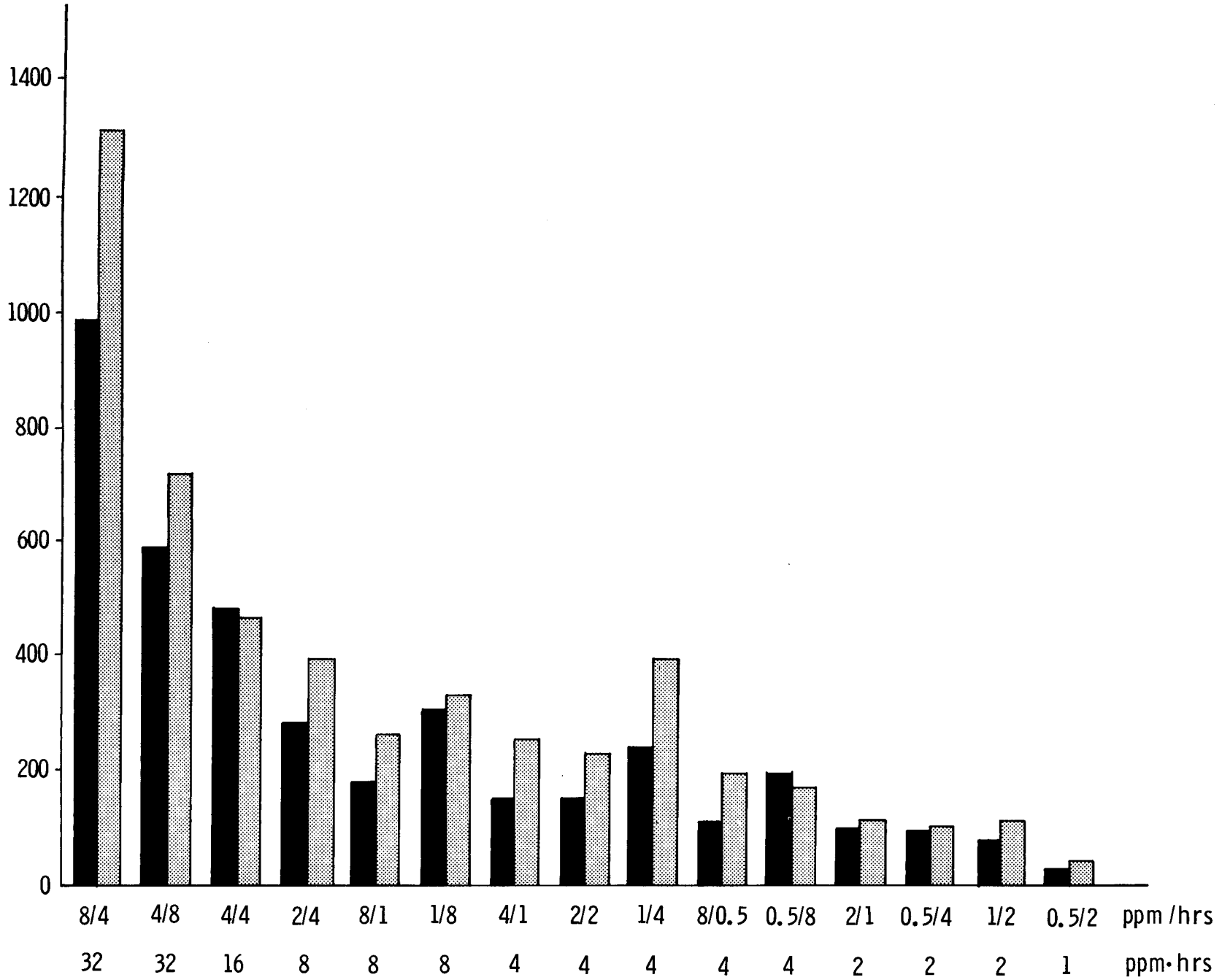

FIGURE 11 FLUORINE CONTENT OF WASHED (SOLID) AND UNWASHED (SHADED) LEAVES OF MELALEUCA AS AFFECTED BY EXPOSURE VALUE

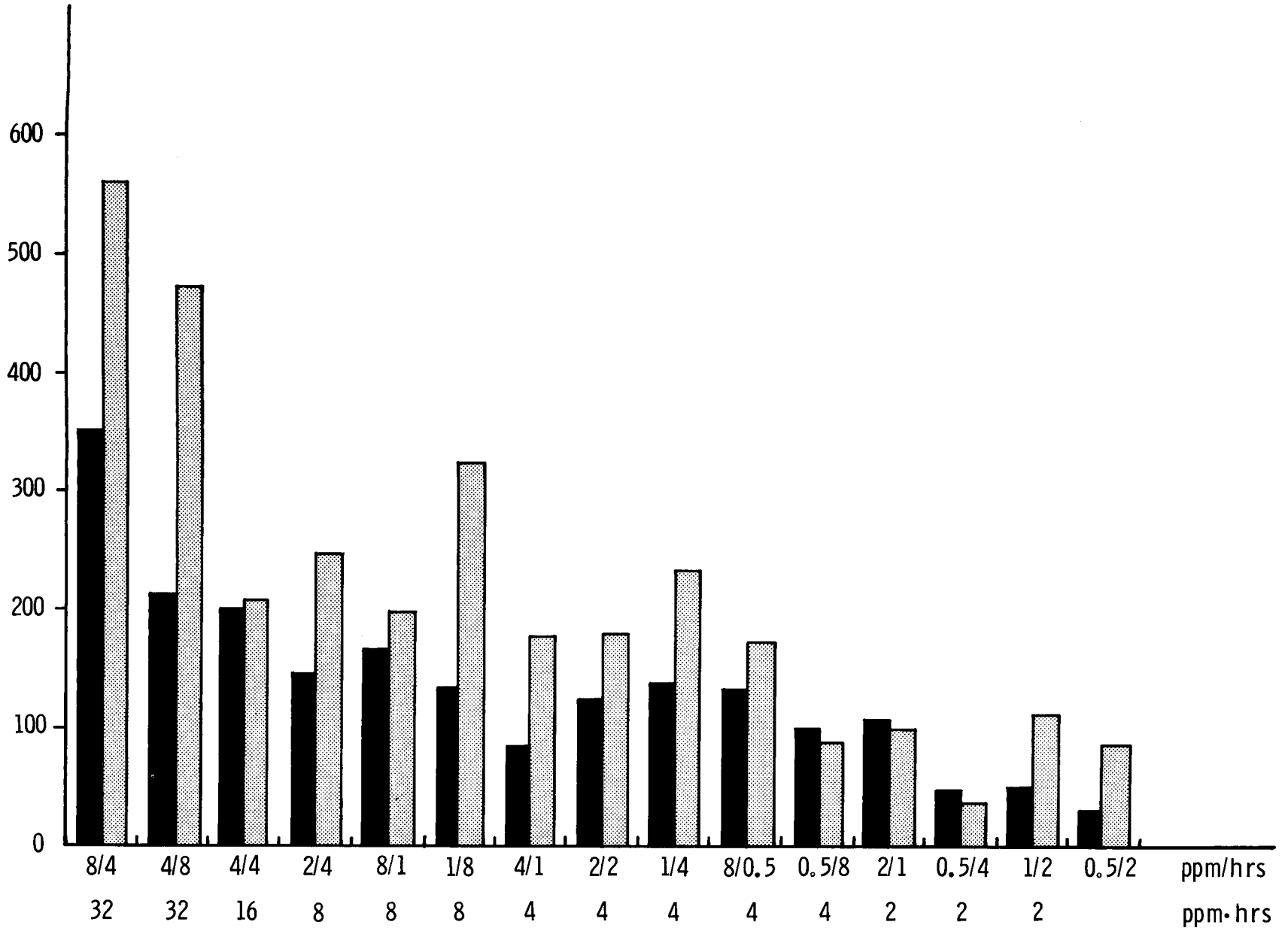

FIGURE 12 FLUORINE CONTENT OF WASHED (SOLID) AND UNWASHED (SHADED) LEAVES OF IXORA AS AFFECTED BY EXPOSURE VALUE

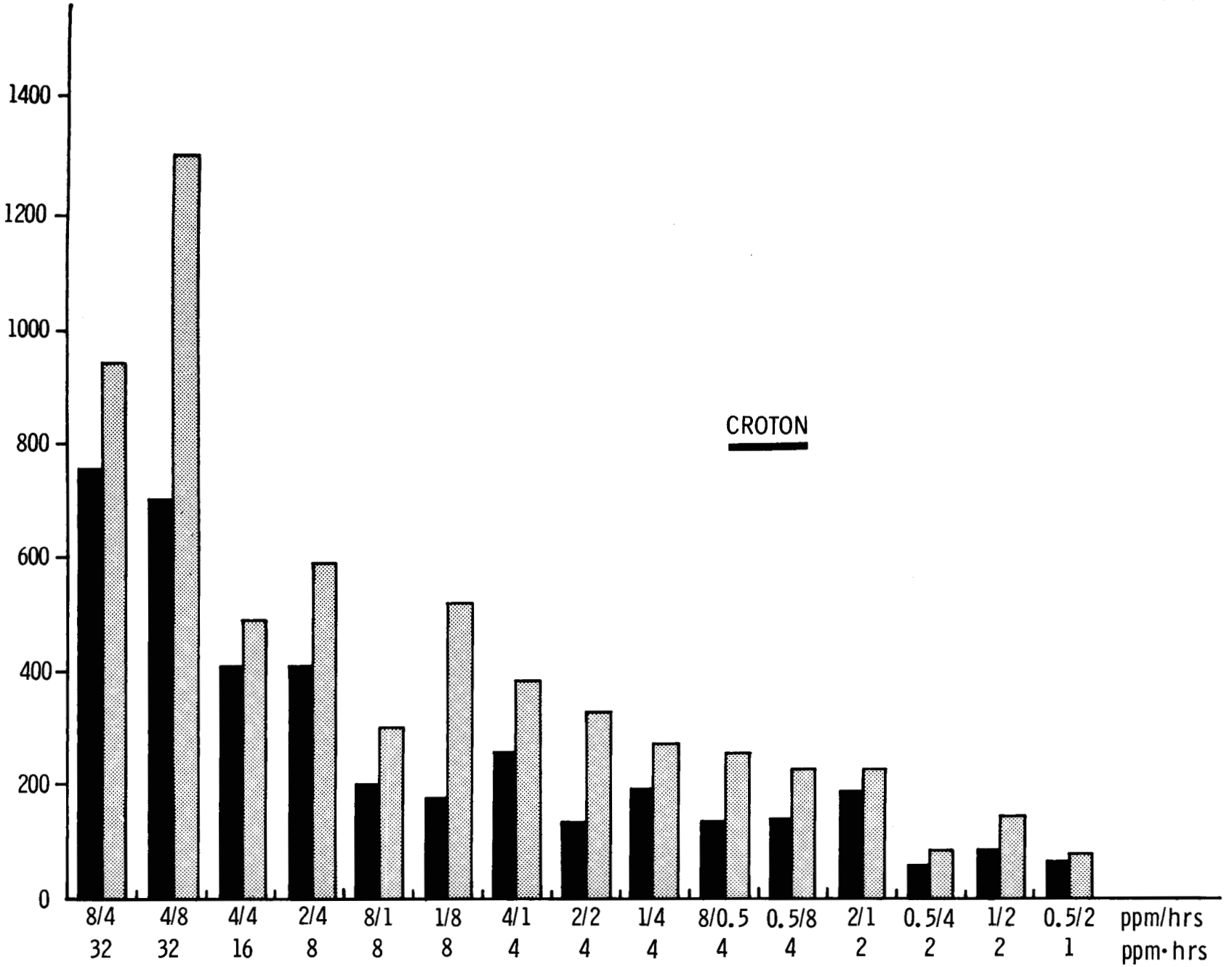

FIGURE 13 FLUORINE CONTENT OF WASHED (SOLID) AND UNWASHED (SHADED) LEAVES OF CROTON AS AFFECTED BY EXPOSURE VALUE

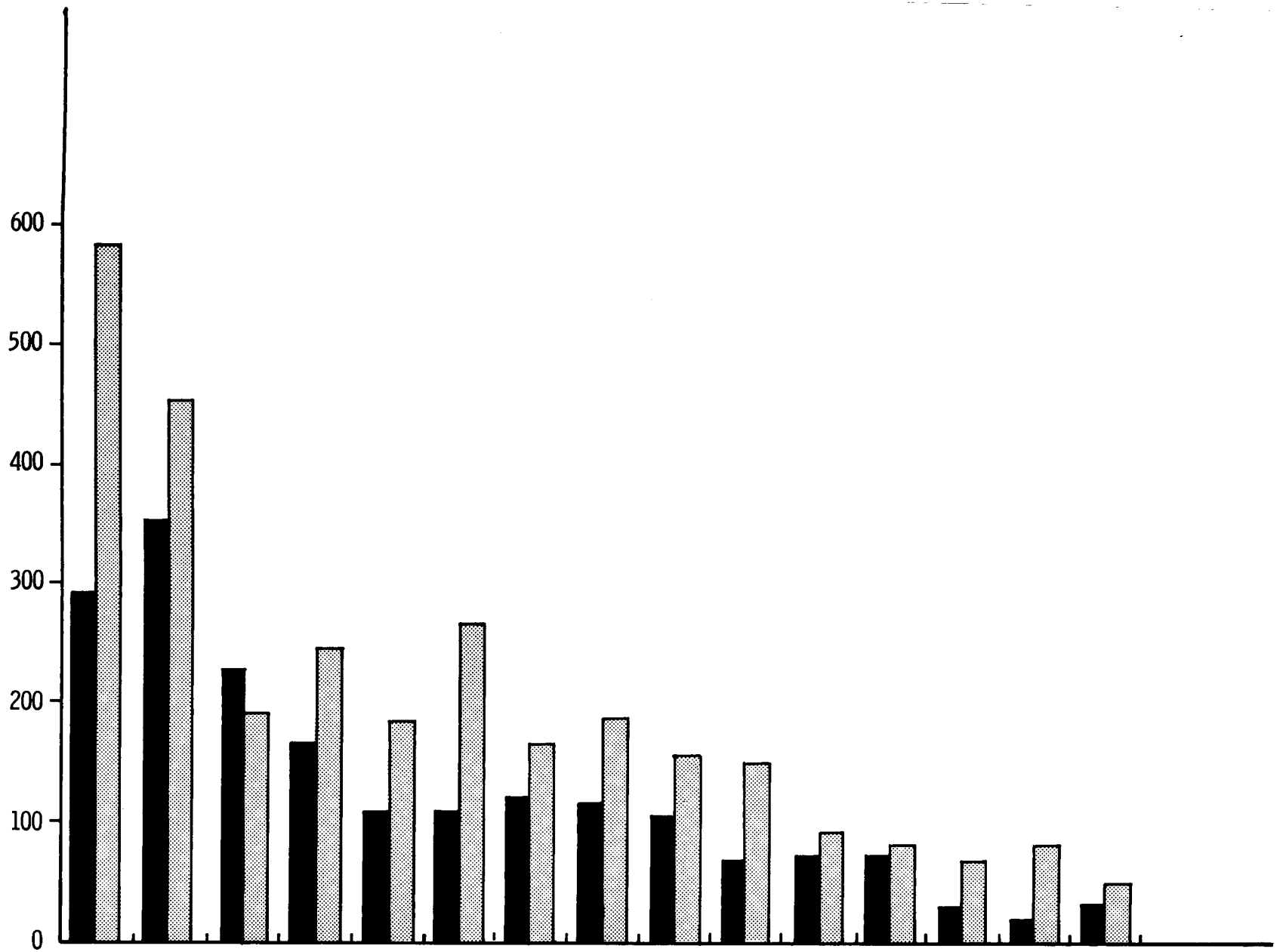

FIGURE 14 FLUORINE CONTENT OF WASHED (SOLID) AND UNWASHED (SHADED) LEAVES OF CARISSA AS AFFECTED BY EXPOSURE VALUE

Unlike HF, NO_2 fumigations result in injury to mature foliage as readily as young foliage, and to intercostal as well as marginal portions of leaves. It is therefore unlikely that this pollutant, after absorption, is transported via the transpirational stream.

In addition to the summaries below, descriptions of the post-fumigation conditions of each citrus variety and ornamental specie injured in the Phase III NO_2 fumigations, are presented in Tables 20 through 30.

5.3.1.1 Citrus Varieties

Injury to citrus by NO_2 was characterized by wilting and defoliation of young leaves. The young leaves that did not abscise and the older leaves showed areas of intercostal and marginal necrosis. The extent of defoliation and necrosis was dependent upon the variety. The varieties are listed below in order of decreasing sensitivity to NO_2:

Marsh Seedless Grapefruit
Pineapple Orange
Valencia Orange
Tangelo Orange
Hamlin Orange
Temple Orange

5.3.1.2 Ornamental Species

Azalea: Plants of this specie were extremely sensitive to NO_2 exposure. The progression of injury was characterized by rapid tissue collapse of leaves of all ages which rapidly became brown-colored followed by necrosis and desiccation. Severe defoliation was common.

Carissa: Carissa plants were insensitive to NO_2 at the exposures provided. Foliar markings observed on NO_2-fumigated plants were of doubtful origin.

Croton: Exposure to 150 ppm NO_2 for four hours and 50 ppm NO_2 for eight hours induced slight intercostal necrosis on leaves of this relatively resistant specie. All other fumigations were without effect.

TABLE 20 SUMMARY OF VISIBLE RESPONSES OF MARSH SEEDLESS GRAPEFRUIT TO 13 NO_2 CONCENTRATION x DURATION EXPOSURES

DURATION (Hours)	NO_2 CONCENTRATION (ppm)					
	25	50	100	150	200	250
0.5			60-70% defoliation of young leaves. Occasional intercostal necrosis of remaining young leaves. 100% fruit abscission.		80-90% defoliation of young leaves; severe necrosis of remaining young leaves, covering 20-80% of leaf surface. Occasional necrotic spots on old leaves. 100% fruit abscission.	
1.0			80% defoliation of young leaves; remaining young leaves severely necrotic. Old leaves not injured.		80-90% defoliation of young leaves; severe necrosis of those remaining. Slight intercostal necrosis of old leaves. 100% fruit abscission.	100% abscission of young leaves and fruit. Slight to moderate necrosis of old leaves.
2.0		50-70% defoliation of young leaves. Slight marginal and intercostal necrosis on remaining young leaves. Moderate to severe fruit abscission.	100% defoliation of young leaves. Slight necrosis of most old leaves. 100% fruit abscission.	100% abscission of fruit and young leaves. Moderate necrosis of old leaves.		
4.0	80% defoliation of young leaves and 100% fruit abscission. Slight to moderate necrosis of old leaves.	80-90% defoliation of young leaves; severe necrosis of those remaining. Old leaves show necrotic spotting affecting up to 10% of leaf surface. 100% fruit abscission.		100% abscission of young leaves and fruit. Some succulent shoots severely necrotic. Moderate to severe necrosis of old leaves.		
8.0	100% abscission of fruit and young leaves. Moderate necrosis of old leaves.	100% abscission of young leaves and fruit. Moderate to severe necrosis of old leaves.				

TABLE 21 SUMMARY OF VISIBLE RESPONSES OF PINEAPPLE ORANGE TO 13 NO_2 CONCENTRATION x DURATION EXPOSURES

DURATION (Hours)	NO_2 CONCENTRATION (ppm)					
	25	50	100	150	200	250
0.5			30% defoliation of young leaves; 50% of those remaining show slight to moderate necrosis. Occasional necrosis on old leaves. Moderate fruit drop.		50% defoliation of young leaves; necrosis of remaining young leaves, up to 30% of leaf surface. Occasional intercostal necrosis on old leaves. 60% fruit abscission.	
1.0			40-50% defoliation of young leaves. Moderate intercostal necrosis on young leaves and occasional necrosis on old leaves.		80% defoliation of young leaves. Moderate necrosis on most remaining leaves of all ages. 100% fruit abscission.	80-90% defoliation of young leaves. Intercostal necrosis on most remaining leaves. 100% fruit drop.
2.0		30% defoliation of young leaves; 25% of remaining young leaves show slight intercostal necrosis. Old leaves not affected.	50% defoliation of young leaves. Intercostal necrotic spots on 10% of leaf surface of most remaining leaves.	60% defoliation of young leaves; remaining young leaves show tip, marginal and intercostal necrosis. Excessive fruit abscission.		
4.0	25% defoliation of young leaves; slight tip necrosis and occasional intercostal necrosis on remaining young leaves. Old leaves not injured.	50% defoliation of young leaves; tip and intercostal necrosis on remaining young leaves. Severe fruit abscission.		100% defoliation of young leaves. Succulent shoots necrotic. Mild to moderate necrosis of old leaves. 100% fruit abscission.		
8.0	40% defoliation of young leaves. 80-90% fruit abscission. Intercostal necrosis of both young and old leaves.	80% defoliation of young leaves. Moderate to severe necrosis of remaining young leaves. Occasional necrosis of old leaves. 100% fruit drop.				

TABLE 22 SUMMARY OF VISIBLE RESPONSE OF VALENCIA ORANGE TO 13 NO_2 CONCENTRATION x DURATION EXPOSURES

DURATION (Hours)	NO_2 CONCENTRATION (ppm)					
	25	50	100	150	200	250
0.5			25% defoliation of young leaves. Occasional necrotic spots on remaining young leaves. 100% fruit abscission.		25-30% defoliation of young leaves. Those remaining show severe tip and occasional intercostal necrosis.	
1.0			50% defoliation of young leaves; remaining young leaves show slight tip necrosis and moderate intercostal necrosis.		50% defoliation of young leaves. Necrosis on remaining young leaves covering up to 40% of leaf surface. 100% fruit abscission.	75% defoliation of young leaves; remaining young leaves severely necrotic. Old leaves not injured.
2.0		40% defoliation of young leaves. Slight necrosis on those remaining. 100% fruit abscission.	60-70% defoliation of young leaves. Moderate intercostal necrosis on remaining leaves. Old leaves not injured.	80% defoliation of young leaves. Remaining young leaves and some old leaves show tip and intercostal necrosis.		
4.0	30-50% defoliation of young leaves; those remaining show intercostal necrosis on 20% of leaf surface.	50% defoliation of young leaves. Intercostal necrosis common on remaining young leaves. Old leaves not injured.		100% defoliation of young leaves. Excessive fruit abscission (up to 100%). Necrotic lesions on many old leaves.		
8.0	50% defoliation of young leaves; tip and intercostal necrosis on remaining young leaves.	80% defoliation of young leaves; severe necrosis on remaining young leaves. Slight necrosis of old leaves.				

TABLE 23 SUMMARY OF VISIBLE RESPONSES OF TANGELO ORANGE TO 13 NO_2 CONCENTRATION x DURATION EXPOSURES

DURATION (Hours)	NO_2 CONCENTRATION (ppm)					
	25	50	100	150	200	250
0.5			30% defoliation of young leaves; 50% of remaining young leaves show mild to moderate necrosis. No fruit abscission.		50% defoliation of young leaves; some succulent shoots show mild necrosis. Mild to moderate necrosis of remaining young leaves. Moderate fruit abscission.	
1.0			30-50% defoliation of young leaves. Many remaining young leaves show moderate necrosis. 50% fruit abscission. Old leaves not injured.		100% defoliation of young leaves. Some succulent shoots severely necrotic. Intercostal necrosis on some old leaves. Severe fruit abscission.	100% defoliation of young leaves. Moderate to severe necrosis of old leaves. 100% fruit abscission.
2.0		Slight abscission of young leaves and fruit. Moderate necrosis on many remaining young leaves (up to 15% of leaf surface). Old leaves not affected.	50% defoliation of young leaves. Many remaining young leaves show moderate necrosis. 50% fruit abscission. Old leaves not injured.	70-80% defoliation of young leaves. Moderate to severe necrosis of remaining young leaves; slight necrosis of old leaves. 100% fruit abscission.		
4.0	20% defoliation of young leaves; remaining young leaves show slight to moderate necrosis. Old leaves not injured.	30-50% defoliation of young leaves. Moderate intercostal necrosis of remaining young leaves. Slight necrotic spotting of old leaves. Moderate fruit abscission.		100% defoliation of young leaves. Moderate necrosis on old leaves. 100% fruit abscission.		
8.0	50% defoliation of young leaves; remaining young leaves show moderate tip and intercostal necrosis. Occasional necrotic spots on old leaves. Moderate fruit abscission.	70-80% defoliation of young leaves. Moderate to severe necrosis of remaining young leaves. Slight necrosis of old leaves. 80-90% fruit abscission.				

TABLE 24 SUMMARY OF VISIBLE RESPONSES OF HAMLIN ORANGE TO 13 NO_2 CONCENTRATION x DURATION EXPOSURES

DURATION (Hours)	NO_2 CONCENTRATION (ppm)					
	25	50	100	150	200	250
0.5			25% defoliation of young leaves; occasional necrotic spots on those remaining. 100% fruit abscission.		30-50% defoliation of young leaves; 50% of remaining leaves show necrosis on 20-50% of leaf surface.	
1.0			Severe defoliation (80-90%) of young leaves. Some necrotic spotting on old leaves. Excessive fruit drop.		100% defoliation of young leaves; occasional necrotic spots on old leaves. 100% fruit abscission.	100% defoliation of young leaves. Moderate intercostal necrosis on older leaves.
2.0		10% defoliation of young leaves. Slight necrosis on both young and old leaves.	Defoliation of 80-100% of all young leaves. Slight intercostal and marginal necrosis on old leaves.	100% defoliation of young leaves; old leaves show slight to moderate necrosis. 100% fruit drop.		
4.0	10-20% defoliation of young leaves. Sporadic necrotic spotting on some old leaves.	25% defoliation of young leaves. Moderate fruit abscission. Slight tip and marginal necrosis on old leaves.		100% defoliation of young leaves. Some succulent shoots also necrotic. Mild to moderate necrosis on old leaves. 100% fruit abscission.		
8.0	40-60% defoliation of young leaves; remaining young leaves show necrosis.	80% defoliation of young leaves; non-specific necrotic areas on remaining leaves. 100% fruit abscission.				

TABLE 25 SUMMARY OF VISIBLE RESPONSES OF TEMPLE ORANGE TO 13 NO_2 CONCENTRATION x DURATION EXPOSURES

DURATION (Hours)	NO_2 CONCENTRATION (ppm)					
	25	50	100	150	200	250
0.5			20% defoliation of young leaves; occasional intercostal necrosis on remaining young leaves; moderate fruit abscission.		25% defoliation of young leaves. 50% fruit abscission. Some succulent shoots necrotic.	
1.0			20% defoliation of young leaves. Mild to moderate tip and intercostal necrosis on 20% of remaining young leaves.		30-40% defoliation of young leaves. Non-specific intercostal necrosis on most fully expanded young leaves. Moderate fruit abscission. No injury on old leaves.	70% defoliation of young leaves; remaining young leaves show moderate intercostal and tip necrosis. Severe fruit abscission.
2.0		10% defoliation of young leaves; occasional tip necrosis on some remaining young leaves. Old leaves not affected.	30% defoliation of young leaves; remaining young leaves show moderate intercostal necrosis.	40% defoliation of young leaves. Necrosis on 10% of leaf surface of remaining young leaves.		
4.0	10% defoliation of young leaves; slight tip necrosis on some remaining young leaves. Slight fruit abscission.	25% defoliation of young leaves. Isolated marginal and intercostal necrosis on remaining young leaves. Old leaves not injured.		50-60% defoliation of young leaves. Intercostal and tip necrosis on remaining young leaves. Some succulent shoots necrotic. 70% fruit abscission.		
8.0	30% defoliation of young leaves. Tip necrosis on 75% of remaining young leaves. Some intercostal necrosis. Old leaves not affected.	40% defoliation of young leaves. Old leaves not injured. Slight fruit abscission. Moderate tip and intercostal necrosis on remaining young leaves.				

TABLE 26 SUMMARY OF VISIBLE RESPONSES OF AZALEA TO 13 NO_2 CONCENTRATION x DURATION EXPOSURES

DURATION (Hours)	NO_2 CONCENTRATION (ppm)					
	25	50	100	150	200	250
0.5			10% defoliation of old leaves; young leaves in tact but severely bronze colored and necrotic		50% defoliation of leaves of all ages. Severe necrosis covering up to 90% of leaf surface on remaining leaves.	
1.0			Moderate defoliation; severe necrosis of all remaining leaves		50-70% defoliation of all leaves. Remaining leaves 100% necrotic.	70% defoliation of all leaves. Remaining leaves 100% necrotic.
2.0		Moderate defoliation. Necrosis of 80% of all leaves ranging from several necrotic spots to complete necrosis. Severity greatest on young leaves.	80-90% defoliation. Remaining leaves 100% necrotic.	All leaves either defoliated or necrotic on 100% of leaf surface.		
4.0	50-70% defoliation of leaves of all ages. 80% of remaining leaves severely necrotic.	70-90% defoliation. All remaining leaves 100% necrotic.		80-90% defoliation. Remaining leaves severely necrotic.		
8.0	80-90% defoliation. Complete necrosis of remaining leaves.	90-100% defoliation of leaves of all ages. Surface of all remaining leaves completely necrotic.				

TABLE 27 SUMMARY OF VISIBLE RESPONSES OF MELALEUCA TO 13 NO_2 CONCENTRATION x DURATION EXPOSURES

DURATION (Hours)	NO_2 CONCENTRATION (ppm)					
	25	50	100	150	200	250
0.5			No defoliation. Severe necrosis of all young leaves and moderate necrosis to many old leaves.		Slight defoliation. Severe necrosis of all young leaves and necrotic spotting on most old leaves.	
1.0			Slight to moderate defoliation. All remaining leaves completely necrotic		Slight to moderate defoliation. All remaining leaves completely necrotic.	Slight to moderate defoliation. All remaining leaves completely necrotic.
2.0		Slight defoliation. Severe necrosis of leaves of all ages.	Slight to moderate defoliation. All remaining leaves completely necrotic.	Slight to moderate defoliation. All remaining leaves completely necrotic.		
4.0	Slight to moderate defoliation. All remaining leaves completely necrotic.	Slight to moderate defoliation. All remaining leaves completely necrotic.		Slight to moderate defoliation. All remaining leaves completely necrotic.		
8.0	Slight to moderate defoliation. All remaining leaves completely necrotic.	Slight to moderate defoliation. All remaining leaves completely necrotic.				

TABLE 28 SUMMARY OF VISIBLE RESPONSES OF HIBISCUS TO 13 NO_2 CONCENTRATION x DURATION EXPOSURES

DURATION (Hours)	NO_2 CONCENTRATION (ppm)					
	25	50	100	150	200	250
0.5			20% defoliation of leaves of all ages. Severe intercostal and marginal necrosis on remaining leaves.		70% defoliation of all leaves. Severe necrosis on 70-100% of all leaf surfaces.	
1.0			70% defoliation of all leaves. Severe general necrosis on remaining leaves.		90% of leaves of all ages either defoliated or completely necrotic	100% of all leaves either defoliated or necrotic and desiccated.
2.0		100% of all leaves either defoliated or necrotic and desiccated.	100% of all leaves either defoliated or necrotic and desiccated.	100% of all leaves either defoliated or necrotic and desiccated.		
4.0	100% of all leaves either defoliated or necrotic and desiccated.	100% of all leaves either defoliated or necrotic and desiccated.		100% of all leaves either defoliated or necrotic and desiccated.		
8.0	100% of all leaves either defoliated or necrotic and desiccated.	100% of all leaves either defoliated or necrotic and desiccated.				

TABLE 29 SUMMARY OF VISIBLE RESPONSES OF IXORA TO 13 NO_2 CONCENTRATION x DURATION EXPOSURES

DURATION (Hours)	NO_2 CONCENTRATION (ppm)					
	25	50	100	150	200	250
0.5			No defoliation. Occasional intercostal necrosis on some old leaves. Chocolate brown discoloration on most leaves.		Slight defoliation of old leaves. Slight intercostal necrosis and chocolate brown discoloration of most old leaves. Slight marginal necrosis of young leaves.	
1.0			Slight defoliation. Slight to moderate intercostal necrotic spotting on old leaves		30-40% defoliation of old leaves. Moderate intercostal necrosis on remaining old leaves.	60% defoliation of old leaves and occasional defoliation of young leaves. Moderate intercostal necrosis on remaining leaves.
2.0		30% defoliation of old leaves. Slight to moderate intercostal necrosis on remaining leaves.	30-40% defoliation of old leaves. Slight to moderate intercostal necrosis on remaining young and old leaves.	50-60% defoliation of old leaves and occasional defoliation of young leaves. Moderate to severe intercostal necrosis of remaining leaves.		
4.0	30-40% defoliation. Slight to moderate necrosis of remaining leaves.	50% defoliation. Moderate intercostal necrosis of remaining leaves.	60-70% defoliation of all leaves. Moderate to severe intercostal necrosis of remaining leaves.	70% defoliation of leaves of all ages. Severe intercostal necrosis of most remaining leaves.		
8.0	50-70% defoliation, especially of young leaves. Moderate to severe necrosis on most of the remaining leaves.	80% defoliation of all leaves. Severe intercostal necrosis of leaves of all ages.				

TABLE 30 SUMMARY OF VISIBLE RESPONSES OF CROTON TO 13 NO_2 CONCENTRATION x DURATION EXPOSURES

DURATION (Hours)	NO_2 CONCENTRATION (ppm)					
	25	50	100	150	200	250
0.5			No visible injury.		No visible injury.	
1.0			No visible injury.		No visible injury.	No visible injury.
2.0		No visible injury.	No visible injury.	No visible injury.		
4.0	No visible injury.	No visible injury.		Slight intercostal necrosis on 10-30% of leaves.		
8.0	No visible injury.	Intercostal necrosis on 20-30% of leaves.				

Hibiscus: Plants of this specie were severely injured by all but the mildest NO_2 fumigations. The first apparent symptoms were intercostal areas of tissue collapse on the upper leaf surfaces only. Within time, these areas became necrotic and were visible on the lower leaf surfaces as well. Relatively high NO_2 exposure induced complete necrosis followed by desiccation and eventual abscission.

Ixora: NO_2-induced damage in this specie was characterized by marginal and intercostal necrosis of leaves of all ages and a chocolate brown discoloration of non-necrotic leaf surfaces. Damage was most severe on older foliage.

Melaleuca: The Melaleuca plants were severely damaged by exposure to NO_2. Injury was characterized by rapid necrosis of leaves of all ages.

All plants survived the 13 Phase III NO_2 exposures. Regrowth from axilliary buds was observed on all plants within three to six weeks after fumigation.

6.0 ECONOMIC AND CIVIL FACTORS

6.1 INTRODUCTION

Past experience in many areas has shown that when air pollution problems occur or are ever suspected, civil problems are created. These may include complaints, claims for damages and litigation. Constraints on air pollution are imposed federally by the Clean Air Act, by state statute, and by local ordinances.

While this program was intended to determine the effects on ecology resulting from a catastrophic spill or fire on the launch complex, its results present more significance to NASA. The results of the HF tests show dramatically that plant damage of major economic and civil significance will be caused by even relatively short-term exposures to concentrations of HF well below those tolerable by humans or animals. Therefore, all operations with fluorine oxidizers will have to be closely examined with respect to air pollution.

6.2 LEGISLATION

The Clean Air Act and its amendments represent major current federal legislation with respect to air pollution. The provisions of this act and, for that matter, of most legislation and controls, are applicable to the control of chronic air pollution.

Under Chapter 170C-9.06 of The Sanitary Code of Florida, entitled "Prohibitive Acts," Florida has established the following regulations covering fluoride emission:

> "170C-9.06 (3) Fluoride Emissions. Unit emissions of fluoride, expressed as pounds of fluoride per ton of P_2O_5, or equivalent, shall not exceed 0.4 (four-tenths) pounds, taking into consideration the following:
>
> (a) Latest advances in the technology of air pollution control.
> (b) The lowest value attained by any operating plant manufacturing similar products.

(c) Existing levels of air pollution in the state.

(d) Location of installation.

The allowable emission of fluorides shall be calculated by multiplying the unit emission specified above times the expressed design production capacity of the installation or plant. Allowable emissions shall be set as low as possible consistent with the above factors."

Further limitations on fluoride emissions have been imposed by the Florida Air Pollution Control Commission. The Rules of the Florida Air Pollution Control Commission state:

"28-3.01 Quantities of fluorides injurious to cattle. ——

(1) Excessive quantities of fluorides in the atmosphere can be dangerous to human, plant and animal life.

Since grass has been accepted as the principal feed for grazing cattle, grass is therefore declared as the medium for determining air pollution. The following are hereby declared to be evidence of air pollution from fluorides as it affects cattle:

(a) A finding by appropriate sampling, and on an average basis, of levels of fluorine in grasses used or to be used as forage or feed is that grasses containing forty (40) ppm fluorine (dry weight basis) will, if consistently used as feed or forage over a substantial period of time, produce harmful effects.

(2) Sampling techniques and methods for analyses, for purposes of both the above and for determining average background, must be standard techniques, published and distributed by the Board.

(3) The fluorine content of grasses shall be, except as hereinafter set out, the content of available fluorine established as follows:

Fluorine content shall be determined from unwashed samples. The average background for natural forage from an uncontaminated area shall be subtracted from the values obtained. Should the adjusted sample contain more than forty (40) and less than eighty (80) ppm, the fluorine content shall be established as follows:

(a) Fluorine content shall be determined from washed samples.

(b) Fluorine content shall be determined on the solution used to wash the samples.

(c) Available fluorine shall be calculated on the basis of one part of washed sample plus one-half of the content found in the washing material.

(4) Where samples of grasses are taken from pastures which demonstrate that there has been an accumulation of fluorine-bearing compounds (such as raw rock phosphate, etc.) in the top or surface soils, or from recently top-dressed soils, then only washed samples will be considered in determining the fluorine content of the grasses so analyzed.

(5) No samples will be taken from improved pastures until a complete ground cover is established; nor shall samples be taken from pastures where applications of phosphate-bearing materials have been applied until a period of ninety (90) days shall have expired after such application.

28-3.02 Quantities of fluorides injurious to gladiolus.——

(1) It is determined that excessive quantities of fluorides in the atmosphere in gaseous forms are injurious to certain vegetation resulting in visible foliage damage. Gladioli are scientifically recognized to be the most susceptible of commercial row crops to fluorine damage. Where gladioli are grown as a commercial crop intending to result in the sale of cut flowers to the public, the following is hereby declared to be evidence of air pollution from fluorides; A finding by analyses in a appropriately taken and washed sample of specific levels of fluorides in the terminal six inches of gladiolus foliage of any variety grown for commercial use when such foliage shall show typical fluoride injury. The standard to be applied shall be that when such analyses reveal in excess of thirty-five (35) ppm fluorides on a dry weight basis, this accumulation shall be deemed to be in excess of soil borne fluorides reaching the foliage through the root system under normal commercial growing practices. Typical visible fluoride injury shall be declared the result of airborne gaseous fluorides.

(2) Where sprays of dusts, labeled as containing fluoride have been used at any time during the cultivation or spray program, plants so sprayed or dusted shall not be sampled."

These limits, principally applicable to the fertilizer industry, can be expected to be even further reduced in the future.

Previous litigation covering air pollution injury was examined to determine if pertinent precedents existed. No precedent which would be of significance to this program was discovered since the majority of litigation is concerned with chronic, rather than short-term, pollution problems.

6.3 ECONOMIC EFFECTS

The results of the experimental program clearly indicate that if relatively low levels of HF or somewhat higher concentrations of NO_2 reach commercial citrus groves, the resultant defoliation, chlorosis and necrosis of the plant tissues will result in partial or complete loss of the crop. The extent of the loss will depend upon the concentration, time of exposure and other factors. If the concentrations reaching the commercial groves are higher than 15 ppm of HF or higher than 250 ppm of NO_2 for 15 minutes during the period of flowering and fruit development, it can be assumed that there would be no commercial citrus crop for that season. Although there is evidence that trees damaged at these levels will renew growth, it may be assumed that detrimental effects will be felt on one or more subsequent crops.

APPENDIX

1.0 FUMIGATION TECHNIQUES

1.1 FUMIGATION CHAMBERS

1.1.1 PHYSICAL DESCRIPTION

The chambers used to conduct the plant fumigations for this study were portable fumigation chambers developed by Boyce Thompson Institute[1] for plant fumigations in the field at low concentrations. Details of construction are shown in Figures 1 and 2.

1.1.2 CIRCULATION

For this program where the propellant concentration levels were extremely high, the chambers were modified to include an air recirculation system and gas scrubber which could be inserted in the recirculation system to remove propellant vapors from the chamber. Figure 3 shows the chamber with the recirculation system and scrubber chamber installed. Figure 4 shows details of the scrubber assembly which was used.

Prior to starting a fumigation, the scrubber was removed from its chamber and the air and propellant vapor circulated freely through the fumigation chamber. As noted in subsequent sections of this appendix, propellant vapor was continuously added through the circulation system to maintain constant levels in the chamber during the fumigation. Upon completion of a fumigation, the recirculating blower was shut off, the scrubber inserted in its chamber and the blower restarted. Vapor concentrations were rapidly reduced to levels which would permit personnel to open the chamber and enter it to remove plant specimens.

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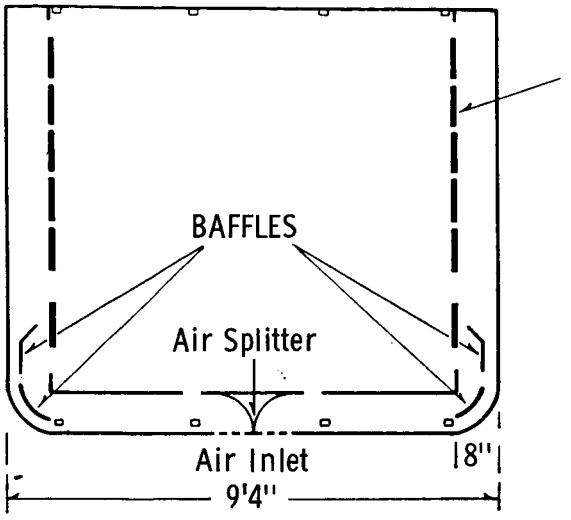
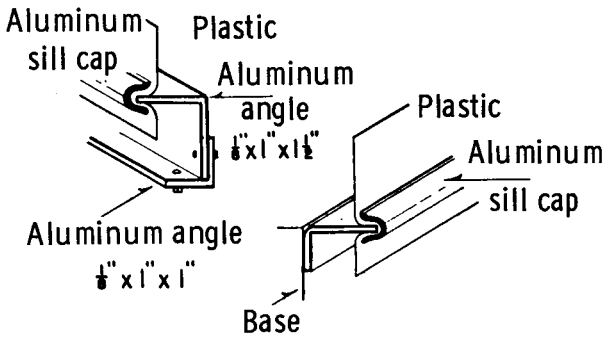
[1] Hitchcock, A.E., P. W. Zimmerman, and R. R. Coe, The Effect of Fluorides on Milo Maize. Cont. Boyce Thompson Inst., 22 (4): 175-206, October-December 1963.





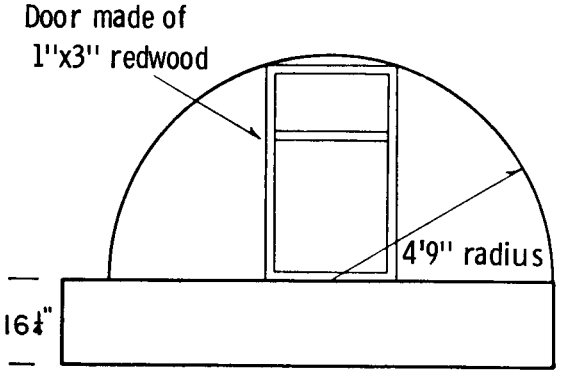
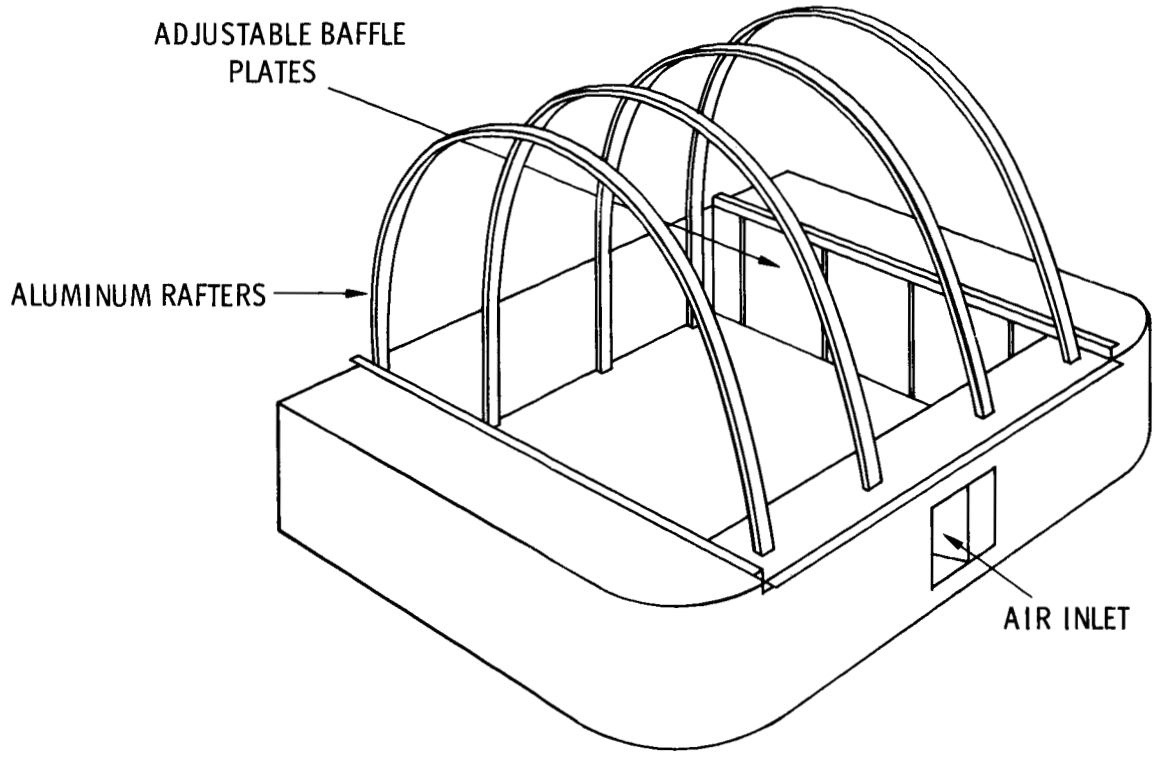


FIGURE 1

FUMIGATION CHAMBER CONSTRUCTION DETAILS (1)



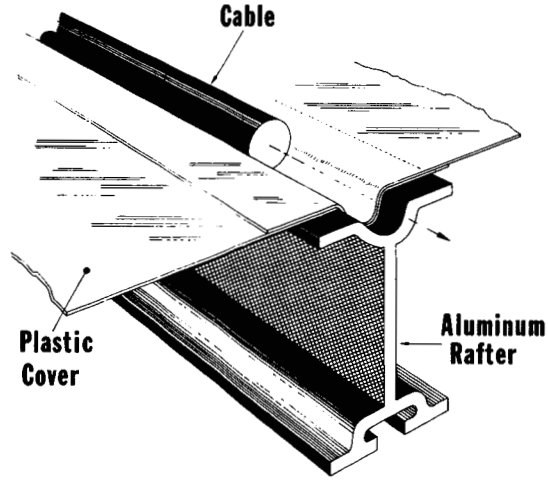


FIGURE 2

FUMIGATION CHAMBER CONSTRUCTION DETAILS (2)

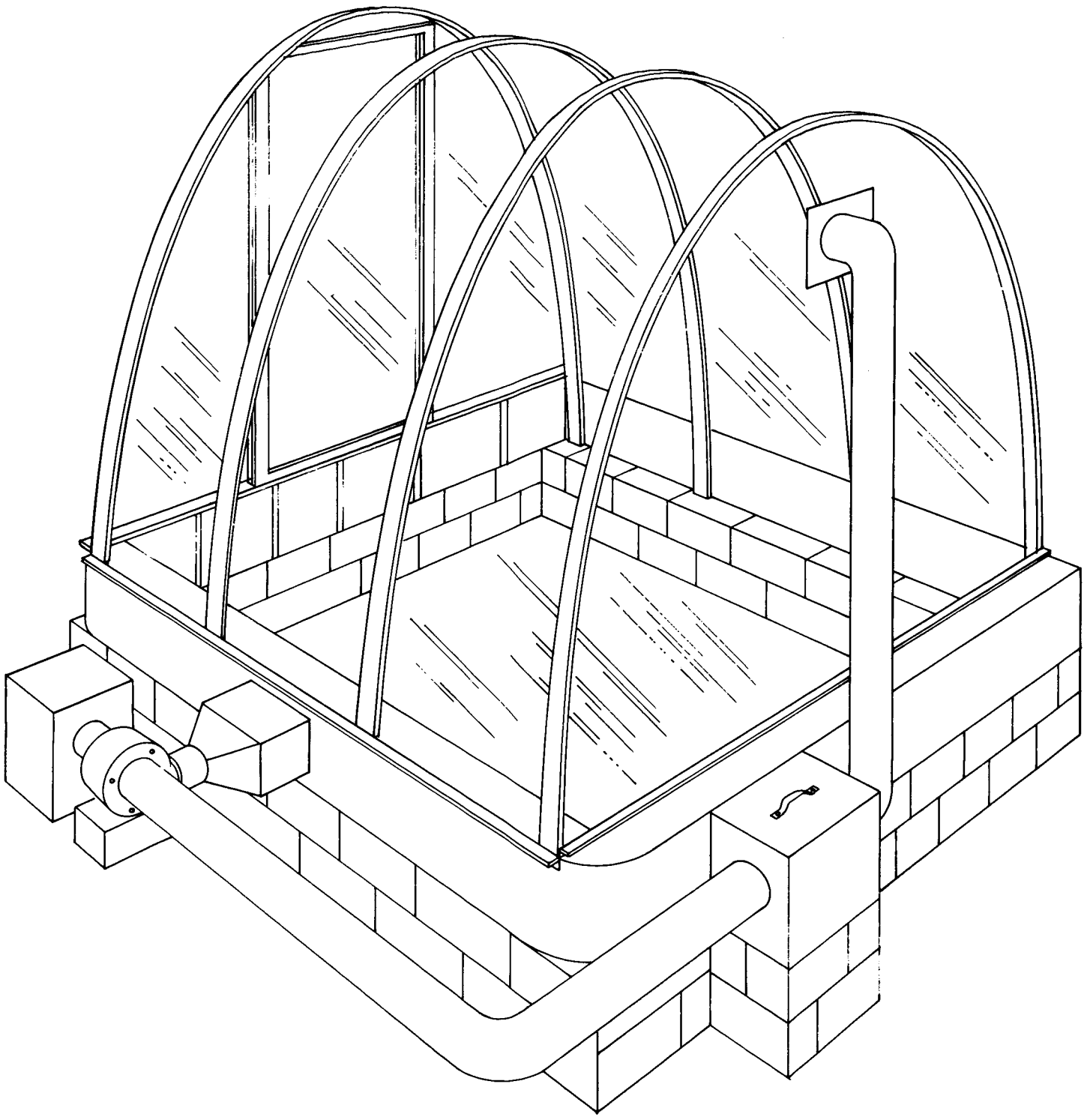
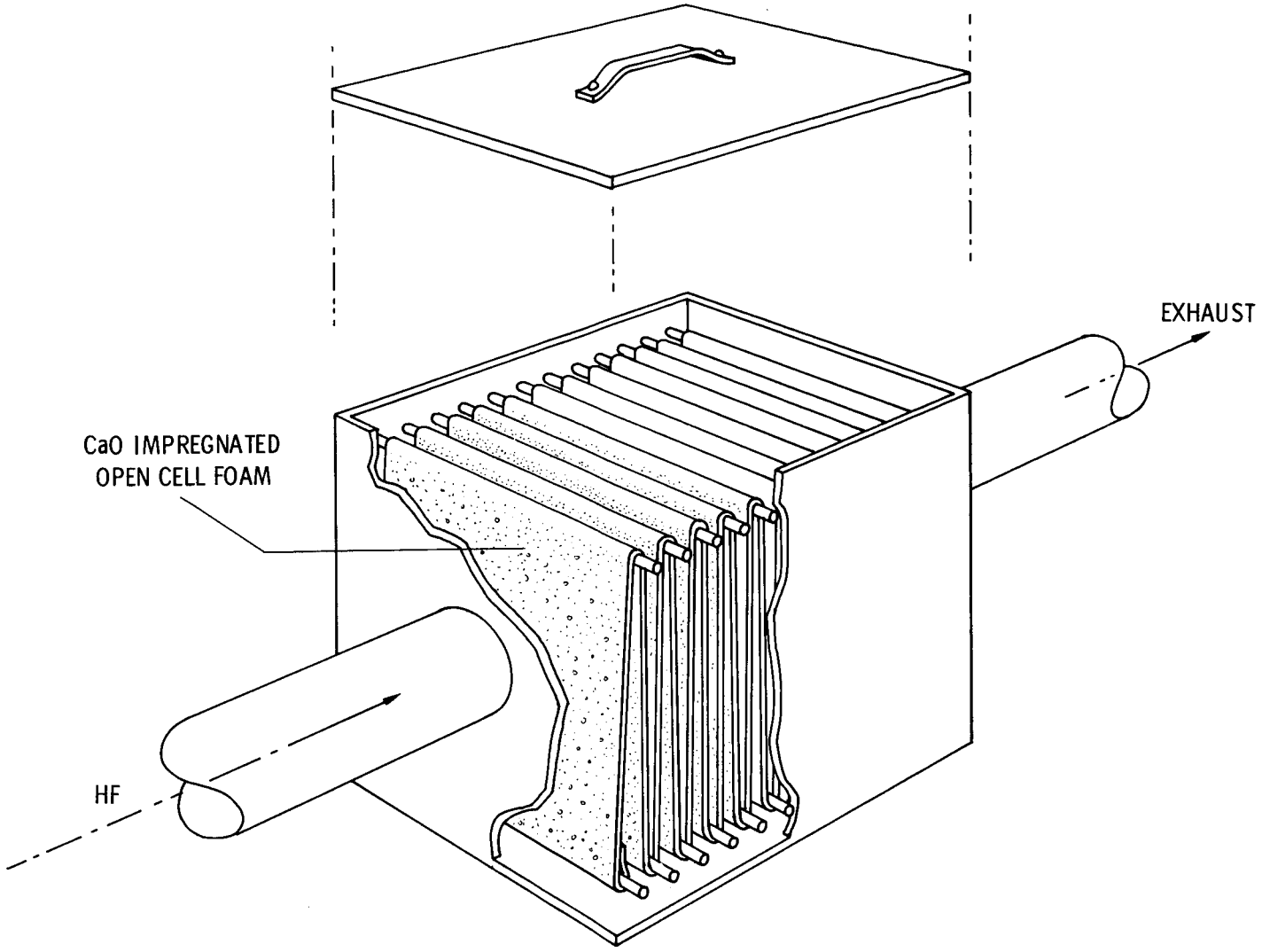


FIGURE 3

FUMIGATION CHAMBER SHOWING RECIRCULATION AND SCRUBBER SYSTEM



SCRUBBER

CUT-AWAY VIEW

FIGURE 4

1.2 HYDROGEN FLUORIDE FUMIGATIONS

1.2.1 INJECTION

To obtain desired HF concentrations within the fumigation chambers, the following procedures and apparatus (Fig. 5) were used.

Aqueous hydrogen fluoride solutions of desired concentration were withdrawn from a reservoir (R) at a known rate by using a proportioning pump[1] (P) and calibrated pump tubes. The solution was pumped into a 1/8-inch I.D. coil of Teflon tubing (C), 25 feet in length immersed in silicone oil[2] bath (B). The temperature of the oil bath was maintained between 180 and 200° C. by means of a thermoregulator (T) and a 750-watt immersion heater (H). Air, supplied by a pump[3] (V) and flowing at eight liters per minute, was also passed through the heated coil of Teflon tubing. The bath temperature, coil length, and air flow rate were such that complete vaporization occurred and only gaseous hydrogen fluoride and water vapor were injected into the air stream of the fumigation chamber blower. The fluoride-laden air was then distributed through the plenum of the fumigation chamber (Fig. 3). Continuous injection of fluoride in conjunction with recirculation of chamber air resulted in a relatively uniform concentration and distribution of the pollutant in the chamber throughout the duration of the fumigation period.

Atmospheric fluoride concentrations can, within limits, be predicted if the air volume within the fumigation chamber, the concentration of the stock solution, and the flow rate at which it is injected into the system are known. The concentration of the stock hydrogen fluoride solution and/or the flow rate can be controlled to achieve desired atmospheric fluoride concentrations. Under the conditions of our experiments,

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1 Technicon Instruments Corp., Ardsley, N. Y.

2 Dow-Corning 200 Fluid (100 cs at 25° C.), Dow-Corning, Midland, Mich.

3 Vacuum and pressure air pump, Gast.

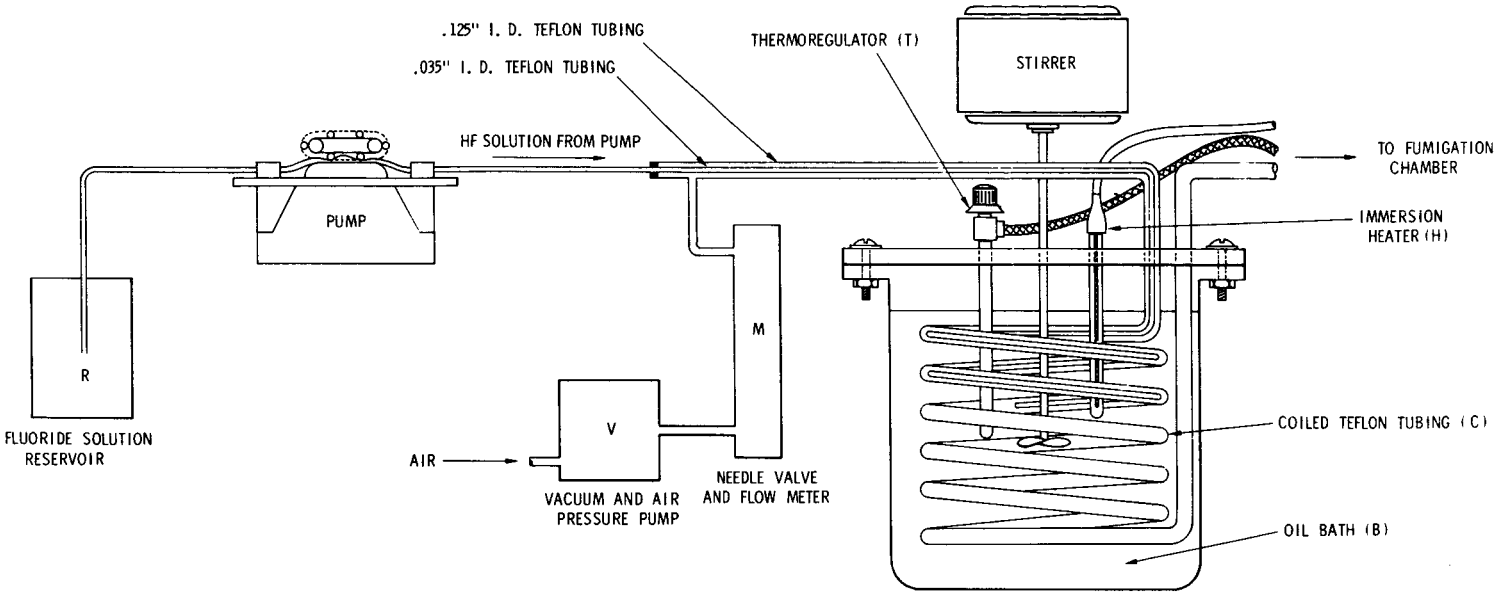

FIGURE 5 DETAILS OF HF INJECTION SYSTEM

the following hydrogen fluoride concentrations were arrived at empirically. Solutions were pumped into the system at 0.8 milliliter per minute to give the desired concentrations of F in the chamber atmosphere.

Desired F Concentration (ppm)	HF Concentration (mg.F/ml.)
0.5	6.25
1	12.5
2	25.0
4	50.0
8	100.0

Upon termination of a fumigation, hydrogen fluoride solution was replaced by distilled water and was pumped through the system for washout. The chamber blower was then temporarily turned off and a calcium hydroxide-impregnated filter, made of polyethylene screening (8 layers), was placed in the return line (see Fig. 4) of the recirculating system. This system was found to efficiently scrub the chamber of gaseous fluoride. The fluoride concentration within the chamber could be reduced from 10.0 to 0.7 parts per mission in 9 minutes.

1.2.2 ATMOSPHERIC MONITORING OF HYDROGEN FLUORIDE

An instrument[4] designed to analyze and record atmospheric sulfur dioxide concentration was adapted to monitor atmospheric hydrogen fluoride. The key component of this instrument is an all glass detecting cell in which a gas sample is drawn through a small orifice suitated just above the reagent[5] liquid, and is thus impelled onto the reagent causing a small depression on the liquid surface. Sulfur dioxide is quantitatively absorbed by the reagent and oxidized to sulfuric acid, causing an increase in electrical conductivity of the reagent. The increase is detected by

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[4] Sulfur Dioxide Analyzer/Recorder, Scientific Industries, Queens Village, N.Y.

[5] 1×10^{-5} $\underline{N}$ H_2SO_4 plus 1×10^{-4} percent H_2O_2 in deionized water.

stainless steel electrodes in the detector cell which are supplied by a high frequency alternating current. The chamges in current are amplified, rectified, and transmitted to the recorder.

The instrument contains a ball-bearing motor-driven diaphragm pump which draws air through the detector cell by way of a needle control valve and flowmeter (0-1.0 cubic feet per hour). The conductivity of the reagent in the detector cell is measured and recorded. The rate of change in conductivity (e.g., the slope on the recorder) is a measure of the sulfur dioxide concentration.

In simplest terms, this instrument measures changes in conductivity of the reagent brought about by changes in acidity. Therefore, it was reasonable to assume that atmospheric fluoride in the parts per million range would also induce conductivity changes of sufficient magnitude to permit its measurement with this instrument if the background sulfur dioxide concentration was low enough to prevent interference.

This hypothesis was tested by using the hydrogen fluoride injection system described above and a small (0.33 m^3) lucite fumigation chamber. Preliminary experiments showed that when the concentration of injected fluoride was increased, a concomitant increase was indicated on the instrument.

To quantitate this sytem, standard curves were derived in the following manner. Solutions containing from 0.1 to 5.0 micrograms hydrogen fluoride per 2 ml. of H_2SO_4/H_2O_2 reagent were placed in the 2 ml. detection cell, and the conductivity of each concentration was determined. The suction pump was not operating during these determinations in order to exclude any ambient sulfur dioxide and/or fluoride. The mean values obtained in this manner at various instrument sensitivity ranges (controlled by selecting different multiplications in the amplifier circuit) are given in Table 1. Standard curves derived from the data of Table 1 are shown in Figure 6. These standard curves were routinely used to convert recorder values (percent) to parts per million F. This was possible because in all air analyses the change in percent of full scale

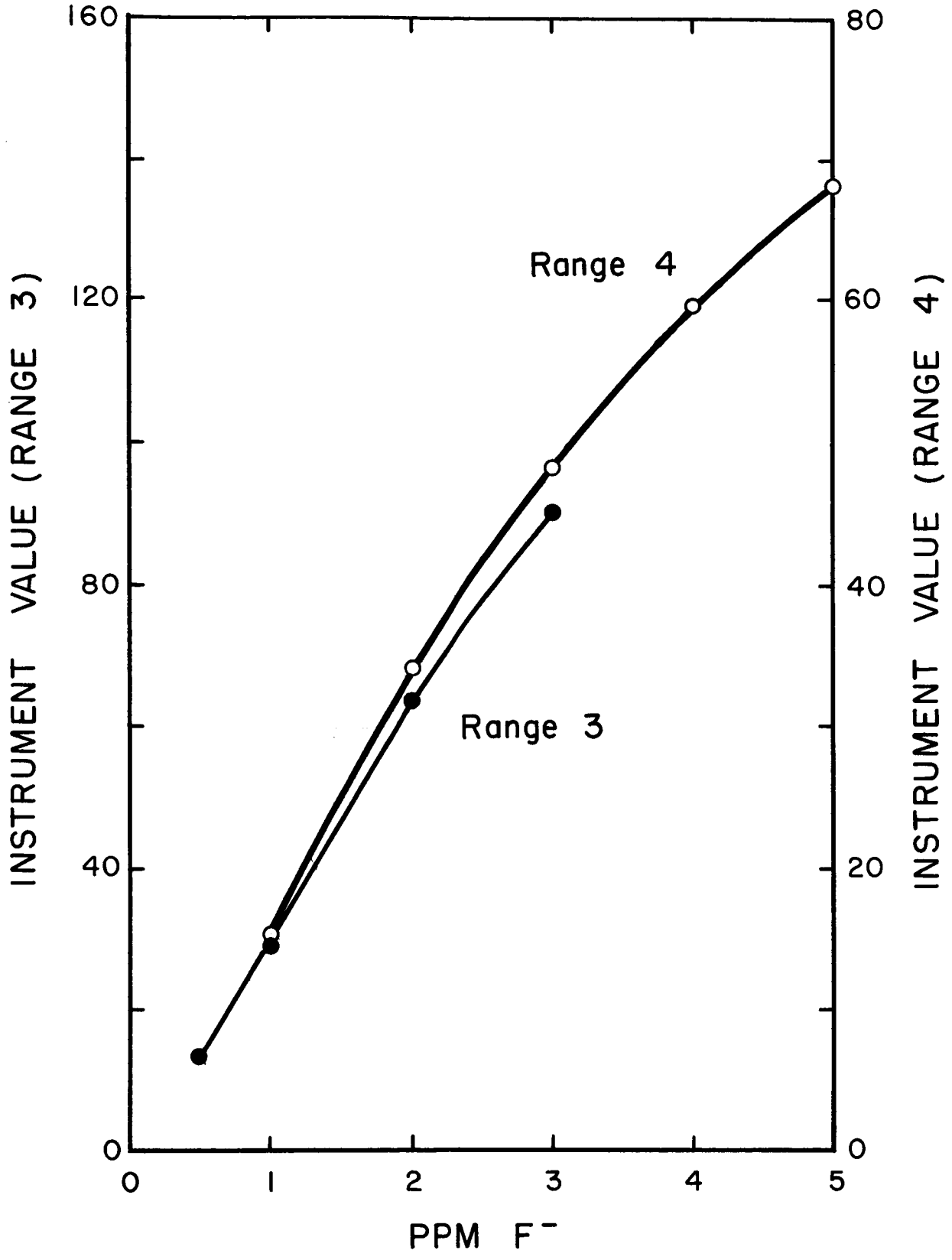


FIGURE 6 STANDARD CURVES USED TO CONVERT ANALYZER/RECORDER VALUES TO PPM F

deflection (slope) induced by drawing air at 300 ml. per minute into the 2 ml. detecting cell was measured over a 3.33-minute period. Thus, one liter of air was collected in the reagent and the milligrams F per liter of air (e.g., parts per million) could be readily computed from the standard curves.

Table 1 Mean values obtained on SO_2 Analyzer/Recorder, expressed as percent of scale deflection, for various hydrogen fluoride concentrations

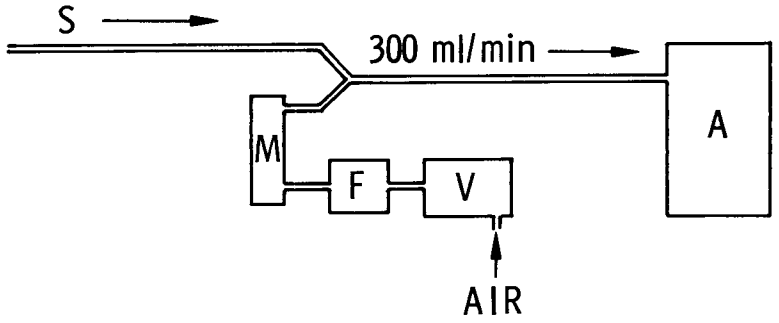
Concentration, ppm.	Range 2	Range 3	Range 4
0.1	19.6		
0.25	24.5		
0.5	74.9	13.3	
1.0		29.0	15.0
2.0		63.9	34.3
3.0		90.0	48.1
4.0			59.4
5.0			68.0

Atmospheric fluoride values obtained using the instrument and the standard curves were essentially the same as those obtained when the gas was trapped in deionized water and titrated with thorium nitrate $[Th(NO_3)_4]$ to a colorimetric end point. The instrument had a further advantage in that it provided a continuous record of the chamber atmosphere.

Pre-fumigation analyses were used to obtain background sulfur dioxide values which were subtracted from subsequent fumigation analyses. Background values ranged from 0.1 to 0.4 parts per million as F.

Direct air analysis for fluoride-laden air was accurate in the 0.5 to 5.0 parts per million range (see Fig. 6). To monitor fluoride-containing atmospheres in the 5 to 10 parts per million range, the chamber air sample was diluted with an equal volume of filtered air. The values

recorded on the instrument were converted to parts per million using the standard curves and then multiplied by two. Dilution was accomplished by inserting a polyethylene "Y" in the chamber sample line through which filtered air was introduced at 150 ml. per minute using a pump, needle valve, and flowmeter (Fig. 7). The instrument pump was maintained at 300 ml. per minute. The difference constituted chamber air. The length of the Teflon tubing between the "Y" and the instrument insured complete mixing of the chamber atmosphere sample with the filtered air prior to its analysis. Experimental determinations substantiated the validity of this dilution method.



A= ANALYZER/RECORDER
S= SAMPLE LINE FROM CHAMBER
V= VACUUM AND AIR PRESSURE PUMP
F= CHARCOAL FILTER
M= NEEDLE VALVE AND FLOW METER

} USED ONLY FOR MONITORING F CONCENTRATIONS GREATER THAN 5 PPM.

FIGURE 7 FLUORIDE MONITORING SYSTEM

1.3 NITROGEN DIOXIDE FUMIGATIONS

1.3.1 INJECTION

Nitrogen dioxide concentrations were achieved by introducing gas from a cylinder containing liquid nitrogen tetroxide (N_2O_4) under pressure through two needle valves (in series) and 1/8-inch I.D. Teflon tubing into the air stream of the fumigation chamber blower. The cylinder was maintained at or above 25° C by means of a flexible heating tape to vaporize N_2O_4 to its gaseous monomer, NO_2. By manipulating the needle valves, the rate of NO_2 injection was manually increased or decreased as dictated by the continuous recording NO_2 monitor referred to in a subsequent section of this appendix. The means of distribution of NO_2-laden air within the chamber was the same as in the fluoride fumigation chambers described above.

1.3.2 NITROGEN DIOXIDE MONITORING

Levels of NO_2 in the fumigation chamber were monitored and recorded using an MSA Portable BillionAire Analyzer and a Bausch and Lomb potentiometric chart recorder.

The BillionAire Analyzer functions by reaching the air-gas sample with a suitable reagent (in this case, diethylamine) and passing this aerosol through an ion chamber where ions are formed by radiation from a radioactive source within the chamber. The ion current produced is a function of the concentration of vapor present and is measured by an electrometer tube and recorded.

For the vapor concentrations and times required for this program, frequent calibration of the instrument and cleaning of the ion chamber were required to maintain instrument response sensitivity.